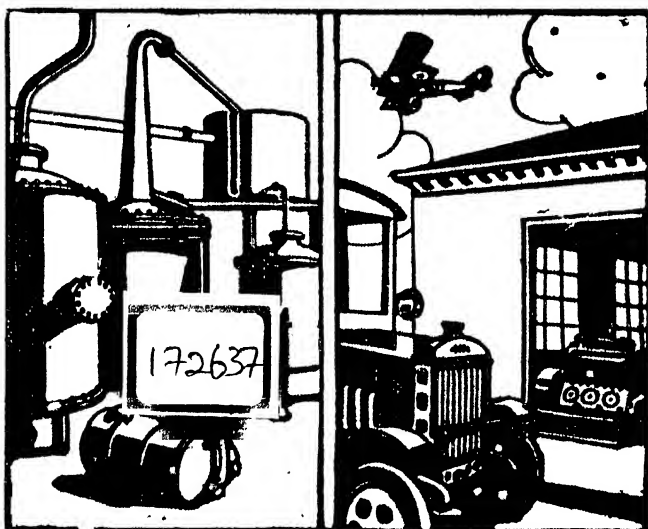
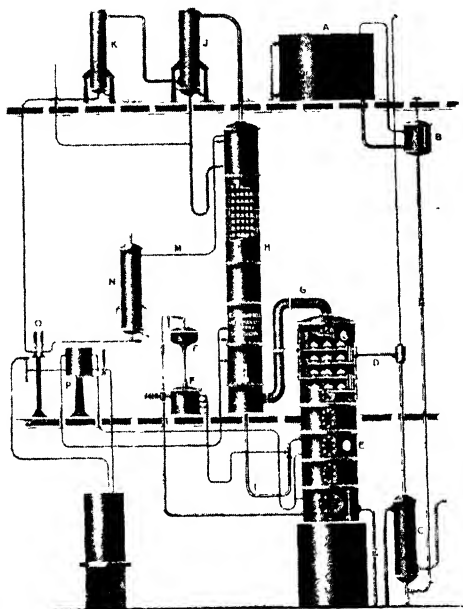


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INDUSTRIAL AND POWER ALCOHOL

THE SOURCES, PRODUCTION, AND DENA-
TURING OF ALCOHOL—ITS MANIFOLD
CHEMICAL AND PHYSICAL APPLICATIONS
IN INDUSTRIES AND MANUFACTURES, AND
ITS USE AS A FUEL FOR INTERNAL COM-
BUSTION ENGINES TECHNICAL, COMMERCIAL,
AND EXCISE ASPECTS OF THE PROBLEM

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PREFACE

THE association of alcohol with conviviality dates back to a very remote period. Its use for other purposes than as a beverage is a development of comparatively recent times and the term "Industrial Alcohol" is even yet the subject of a good deal of misconception. The Government Committee on the Utilization of Alcohol for Power Purposes (1919) indeed mentioned that some sections of the community believed that the words "industrial alcohol" referred to an inferior spirit for drinking purposes. One of the objects of this small work is to give an indication of the widespread chemical and industrial uses to which alcohol can be applied, including medicinal products, dyes, photographic materials, celluloid, and fine chemicals of all sorts.

Apart, however, from these manufactures, a new aspect of the subject has sprung up in recent years, which calls insistently for supplies of alcohol far in excess of anything that has been attained hitherto. The advent of the internal combustion engine gave rise to a demand for enormous quantities of liquid fuel; the earth has been tapped for petroleum fuel with a prodigality which cannot continue. The whole world's supply of petroleum is small when considered in comparison with the supply of coal. Already the demand is outstripping the supply, with consequent rise of price. The increasing home-needs of America leave less and less for export, and we shall be faced in the near future by a serious check to the development of motor-transport.

In this book an attempt is made to show to what extent alcohol forms a suitable substitute for petrol, and to examine into the possible sources of alcohol,

in order to ascertain the prospects of obtaining it in abundance, at a price which will compete with that of petrol. The desirability of drawing our supplies of motor fuel from recurrent vegetable sources instead of from the world's fixed capital of mineral wealth is obvious.

"Power-alcohol" is a subject which affects every one in the community, determining as it does the cost of road-transport for goods and passengers, and of tractors for agriculture and other purposes which go right to the root of our every-day needs. The time is not yet ripe to say with certainty whether alcohol will form the main fuel of the future, but research in this direction is of the highest importance for the future of the internal combustion motor.

R. C. FARMER.

LONDON.

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INDUSTRIAL AND POWER ALCOHOL

CHAPTER I

INTRODUCTORY

ALCOHOL has been known from time immemorial for drinking purposes. It is readily produced, in a dilute condition, by the fermentation of various fruit juices, and the process of distillation has also been known for many centuries. It was not, however, until the nineteenth century that other uses for alcohol began to emerge. A necessary preliminary to such applications was a knowledge of the method of obtaining a concentrated alcohol from the weak spirit by distillation with some form of fractionating column which separated the alcohol distillate from the water. When it became possible in this way to obtain alcohol up to about 90 per cent. strength, this was found to possess very valuable solvent properties, which made it a suitable substance for the manufacture of varnishes, etc.

Meanwhile, alcohol for drinking purposes had been made a subject for taxation, and the duties were too high to permit of the use of spirits for industrial purposes. This state of affairs reached its climax about 1853 when the demand for concessions as regards the duty on spirit for industrial purposes became very insistent. This was met in 1855 by adding nauseous substances to the alcohol to be used for industrial purposes so as to render it undrinkable. Wood naphtha was mainly used for this purpose,

and the alcohol thus "methylated" was allowed to be free of duty. The example thus set by Great Britain was followed in due course by most other countries, and has on the whole served its purpose well, though, as at present administered, it is open to some criticism (Chapter III).

During the second half of the nineteenth century the uses of alcohol were greatly extended, and it became very important, not only as a solvent, but also for the manufacture of many drugs, dyes, and fine chemicals. These uses were developed much more in Germany than in Great Britain. Thus in the period immediately before the war (1909 to 1913), 42 per cent. of the alcohol produced in Germany was used for technical purposes, whereas in the United Kingdom the proportion was only 15 per cent.

Power-alcohol. The above applications, important as they are, have never caused any serious shortage of alcohol; it has always been possible to manufacture enough alcohol for drinking purposes in addition to that required for technical purposes. During the last few years, however, forces have been coming into play which are rapidly altering this state of affairs. The rapid development of internal combustion engines, requiring a volatile liquid fuel, is leading to an ever-increasing shortage of petrol, and the necessity for a substitute for petrol is becoming very urgent. The price of petrol has risen 300 per cent. in 15 years, and limitations to the world's supply are becoming distinctly visible. Compared with coal, petroleum is by no means a plentiful fuel; the world's production is stated to be only equal to 27 per cent. of the coal output of the British Isles. The volatile petrol fraction forms on an average only some 6 to 8 per cent. of the petroleum. If the demand continues to increase as at present, the shortage will become very acute in a few years.

The problem of finding a substitute for petrol is

not an easy one. Last year we imported over 200,000,000 gallons of petrol (about 60 per cent. from America). To replace any large proportion of this by other fuels is a difficult matter. Benzol (obtained from coal tar by distillation) is already being used to the limit of its resources. The production of benzol, together with the shale fuels, was given in 1919 as only 30 million gallons. Already the use of benzol has forced its price up in about the same ratio as that of petrol, and has handicapped its use for other technical purposes. Of the few other liquids which offer any promise as substitutes for petrol as motor-fuel, alcohol stands out, as the one which may with some degree of probability be obtainable in quantities sufficient to cope with the demands. This will necessitate enormous extensions to the present sources of supply, the pre-war production of alcohol in this country (namely, 26 million gallons a year) being only about one-eighth of the quantity of petrol imported in 1919.

We have to enquire, therefore, on the one hand, into the possibilities of finding prolific and cheap sources of alcohol, and on the other hand, into the suitability of alcohol as a motor-fuel.

Sources of Alcohol. The sources of alcohol, existent and potential, are dealt with in Chapters IV and V. We have as the present universal source the fermentation of various vegetable products and, in considering the possibilities of increasing the supply therefrom, we have to guard against encroaching on the supply of food. The enquiry resolves itself, therefore, into a search for the most prolific plants from which alcohol can be readily obtained. Many researches have been made in this direction, and the general result is to show that there are very great undeveloped resources from which alcohol may be obtained by fermentation. Opinions are divided as to whether the demand

for alcohol-fuel can be met completely in this way, but it appears at least probable that much could be done in this country by a systematic reclamation of waste land, and that if a co-operative system were introduced, similar to that which has long been in use in Germany, the growth of potatoes or other crops for the production of alcohol could be stimulated greatly, and at the same time the country would be provided with a potential stock of food in case of emergency.

Apart from this, a review of the vegetable products of different parts of the world indicates that we may look to such plants as the Indian bassia tree, sorghum, cassava, and the nipa palm for at least a partial solution to the problem. The more complete utilization of wood (in the form of sawdust or shavings) for making alcohol still requires much research, but if investigations at present in progress on the action of moulds on sawdust prove successful, a further valuable source of alcohol will be made available.

Synthetic Alcohol. Apart from fermentation-alcohol, we have also the possibility of synthetic alcohol (Chapter V). Two main sources present themselves. One of these is the ethylene which can be extracted from coke-oven gas and coal gas. It is estimated that if the whole of the coal gas and coke oven gas were treated in this way, some 50 million gallons of alcohol per year could be obtained. In practice the manufacture would doubtless be confined to the larger works, and the above figure is therefore an optimum. The work in this direction is not sufficiently far advanced to show the cost of the alcohol, but further investigation is very desirable. The other source of synthetic alcohol, namely, calcium carbide, is of less interest in this country, as carbide is naturally made most cheaply in countries where water power is available. Developments in this

direction might, however, meet with success in some of the Dominions.

Use of Alcohol in Motors. The suitability of alcohol as a motor fuel has been the subject of considerable investigation (Chapter VIII). The main result of this has been to show that alcohol can take the place of petrol with certain modifications in the engine. It is important to observe that, as all our previous experience has been with petrol as fuel, the internal combustion engine has been gradually adapted to give the best results with petrol. The comparisons of alcohol with petrol are liable, therefore, to favour the latter, and it is reasonable to suppose that with further development, the alcohol-engine will reach a degree of perfection comparable with the petrol-engine.

Comparison of Alcohol and Petrol. The main points in which alcohol differs from petrol may be summarized as follows—

(1) The vapour pressure of alcohol at low temperatures is lower than that of petrol. In consequence of this the alcohol-motor is more difficult to start. To remedy this, the motor may be started on petrol and then switched over to alcohol, or the alcohol may be mixed with benzol, ether, etc.

(2) Alcohol takes longer to burn to explosion than petrol; hence the alcohol-motor should have a higher compression and a longer stroke than the petrol motor.

(3) The mixture of alcohol vapour and air can safely be subjected to a pressure of 200 atmospheres whereas the safety-limit for petrol is 80 atmospheres.

(4) Mixtures of alcohol vapour and air have a wider explosive range than is the case with petrol. This permits of greater latitude in the air supply.

(5) Alcohol vapour requires less air for its combustion than petrol vapour. A consequence of this is that more complete mixing occurs in the case of alcohol and the combustion is much more complete. This increases the efficiency, and renders the exhaust gases smokeless and almost inodorous, except in so far as lubricants give rise to contamination.

(6) The heat of combustion of alcohol is much lower than that of petrol. This disadvantage is, however, largely compensated by the more complete combustion of alcohol. Comprehensive trials under practical conditions show that a mixture

of equal parts of alcohol and benzol gives results which compare favourably with those of petrol as regards thermal efficiency.

(7) Alcohol may give rise to small quantities of acetic acid if the combustion is incomplete, and this may cause corrosion of metal surfaces. In some cases ammonia has been added to counteract this by neutralizing the acid.

(8) Alcohol is miscible with water. This renders it safer in case of an accidental fire, but this advantage disappears if it is stored as a mixture of alcohol and benzol. Any small quantity of water finding its way into a storage tank mixes at once with alcohol, and does not seriously affect its use as a motor fuel.

Alcohol has been in use for some considerable time for agricultural engines, and in some countries for motor purposes. In Germany it was used to a large extent during the war. It is in use in South Africa and Australia. In America it is used for the aerial postal service, and other countries are likely to adopt it before long as a motor fuel.

Excise Restrictions. One factor which impedes the development of power-alcohol in this country is the existence of excise restrictions framed many years ago before power-alcohol entered into consideration (Chapter III). These restrictions also hinder the introduction of the most up-to-date and economical methods of manufacture of alcohol. The main subjects of criticism are---

(1) The prohibition of brewing and distilling simultaneously, with consequent curtailment of output.

(2) The necessity of stopping work at week-ends, thus precluding continuous processes.

(3) The regulation as to the use of the saccharometer, which prevents the introduction of the most economical methods of fermentation.

(4) The prohibition of the working of by-products.

(5) The refusal to permit transport of alcohol by tank-wagons.

(6) The regulation precluding the denaturing of alcohol in a vessel already containing any denatured alcohol.

(7) The limitation to 4 gallons of the quantity of spirit which may be bought at one time, and the small maximum stock which may be held by the retailer.

(8) The large proportion of wood naphtha in mineralized methylated spirit, which is stated to cause corrosion of the engines.

(9) The high cost of denaturing, by the only methods at present permitted by the regulations.

(10) The refusal to recognize methylation of alcohol carried out before importation.

Various other points are also criticized. To a great extent it is a question of a suitable denaturant. If a more effective denaturant could be found, various restrictions could be relaxed with safety, and attempts are being made in this direction.

In the interim report of the Committee on the Use of Alcohol for Power Purposes (1919), the harmful effect of the excise restrictions is recognized, and recommendations are made as to the relaxation of certain of these.

Summary. Briefly, therefore, the use of power-alcohol depends upon—

- (1) Its suitability as a fuel.
- (2) Its production in sufficient quantities.
- (3) The removal of restrictive regulations.

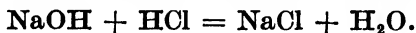
The first of these may be said to be solved, though further research will certainly lead to improvements. The third will doubtless yield in time to the force of public opinion. The second forms the crux of the problem, and its solution cannot be said to be in sight, but the indications are sufficiently promising to warrant every encouragement.

CHAPTER II

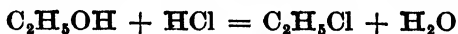
THE CHEMICAL AND PHYSICAL PROPERTIES OF THE ALCOHOLS

The Alcohol Series. The term alcohol is commonly applied to the spirit obtained by the ordinary fermentation process from sugars. In chemistry, however, the word has a wider application ; just as there are ~~many~~ "sugars," apart from the ordinary sugar used for food purposes, so also there is a whole series of "alcohols" of which ordinary alcohol forms one of the members. Several other members are also of industrial importance, and as it will be necessary to refer to certain of these, a short description of their chemical nature will be of assistance in appreciating their industrial applications.

The alcohols are characterized by the fact that they contain a hydroxy group, OH, attached to a carbon atom, and that this hydroxy-group can be replaced by acid radicles. This may perhaps be made more plain by analogy with an inorganic hydroxide, such as sodium hydroxide, NaOH. When sodium hydroxide reacts with an acid, such as hydrochloric acid, the hydroxy group is replaced by the acid radicle, as expressed by the equation—



Ordinary alcohol is ethyl hydroxide, $\text{C}_2\text{H}_5\text{OH}$, and this reacts also with hydrochloric acid as follows—



Ethyl
alcohol

Ethyl
chloride

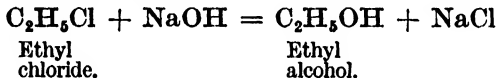
In the same way, ethyl alcohol can react with

other acids to form "ethereal salts" or "esters." Thus we have—

Sodium acetate, $\text{CH}_3\cdot\text{COONa}$.	Ethyl acetate, $\text{CH}_3\cdot\text{COO}\cdot\text{CH}_2\cdot\text{CH}_3$.
" benzoate, $\text{C}_6\text{H}_5\cdot\text{COONa}$.	" benzoate, $\text{C}_6\text{H}_5\cdot\text{COO}\cdot\text{CH}_2\cdot\text{CH}_3$.
" oxalate, COONa .	" oxalate, $\text{COO}\cdot\text{CH}_2\cdot\text{CH}_3$.
" oxalate, COONa .	" oxalate, $\text{COO}\cdot\text{CH}_2\cdot\text{CH}_3$.

and many others. Ethyl hydroxide differs from sodium hydroxide in that it has no alkaline reaction. There is also the important practical difference that, whereas sodium hydroxide reacts instantaneously and completely with acids, ethyl hydroxide (alcohol) reacts only slowly and incompletely. In order to make the reaction more rapid and complete, it is a common practice to add some strong sulphuric acid to take up the water which is formed.

It should be mentioned that the esters can also be re-converted to the alcohols by the action of sodium hydroxide—



These reactions are common to the whole series of alcohols of which the following are the best-known—

CH_3OH	Methyl alcohol, or wood spirit.
$\text{C}_2\text{H}_5\text{OH}$	Ethyl alcohol, the ordinary alcohol.
$\text{C}_3\text{H}_7\text{OH}$	Propyl alcohol, in fusel oil.
$\text{C}_4\text{H}_9\text{OH}$	{ Butyl alcohol, obtainable by a special fermentation process.
$\text{C}_5\text{H}_{11}\text{OH}$	Isobutyl alcohol, in fusel oil.
	Isoamyl alcohol, the main constituent of fusel oil.
$\text{C}_3\text{H}_5(\text{OH})_3$	Glycerol.
$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	Benzyl alcohol.

The alcohols also include the sugars, cellulose starch, and many other vegetable products which contain a replaceable hydroxy-group, but which do not come within the scope of the present subject.

The subdivisions of alcohols into primary, secondary, and tertiary need not be entered into in detail, as we are concerned only with primary alcohols. It will suffice to show by their constitutional formulae the structures of the three types—

	Typical Group	Example
Primary alcohols	$\cdot\text{CH}_2\text{OH}$	$\text{CH}_3\cdot\text{CH}_2\text{OH}$
Secondary „	$:\text{CHOH}$	$(\text{CH}_3)_2:\text{CHOH}$
Tertiary „	$:\text{COH}$	$(\text{CH}_3)_3:\text{COH}$

We may now turn to ethyl alcohol, the best-known representative, and consider its general properties. As regards its chemical behaviour, the information may be taken as typical, and applicable to the other primary alcohols, but the physical properties such as boiling point and specific gravity are different for the individual alcohols. Table I shows the most important physical properties of the common alcohols. A few hydrocarbons are added for convenience in comparing the properties which have a bearing on the use of alcohol for power purposes.

Ethyl Alcohol, $\text{CH}_3\cdot\text{CH}_2\cdot\text{OH}$. This is generally known in a dilute condition for beverages, and in the mixture containing some 80 to 90 per cent. of alcohol known as methylated spirit. When pure, ethyl alcohol forms a colourless liquid having a slight, agreeable odour, and burning with a pale blue, non-luminous flame. It boils at $78\cdot3^\circ\text{C}$, and melts at -117°C . The specific gravity of pure alcohol is $0\cdot79359$ at $15\cdot6^\circ\text{C}$, compared with water at $15\cdot6^\circ\text{C}$. The specific gravity of aqueous solutions varies according to the concentration, and this forms a most important method of ascertaining the alcohol-content. Space does not permit of full tables of the specific gravities of aqueous solutions, but an abbreviated table is given in the Appendix.*

* For fuller tables see Simmonds' *Alcohol*, pp. 237-257.

TABLE I.—PHYSICAL PROPERTIES OF VARIOUS ALCOHOLS AND HYDROCARBONS.

NAME.	Formula.	Molec. Weight.	Sp. gr. $\frac{4}{4}$	M.P. $\frac{4}{4}$	B.P. $\frac{4}{4}$	Solubility in Water.	Refractive Index $\frac{H}{a}$	Vapour pressure at 10°C.	Specific Heat.	Heat of Evaporation.	Heat of Formation.
				°C.	°C.			mm. Hg.	cal. per gram.	cal. per gram.	
Alcohols—											
Methyl alcohol	CH_3OH	32	0.796 (20/4)	-95	66	miscible	1.328 (20)	50.1	0.59	269	61.7
Ethyl alcohol	$\text{CH}_3\text{CH}_2\text{OH}$	46	0.789 (20/4)	-117	78.3	"	1.359 (20)	23.8	0.65	206	69.9
Propyl alcohol (norm.)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	60	0.804 (20/4)	—	97.4	"	1.382 (20)	7.4	0.67	166	78.6
Isopropyl alcohol	$\text{CH}_3\text{CHOHCH}_3$	60	0.789 (20/4)	-86	82.7	"	1.376 (20)	—	0.53	161	80.6
Butyl alcohol (norm.)	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	74	0.810 (20/4)	-80	116.8	8%	1.397 (20)	—	0.69	143	—
Isobutyl alcohol	$(\text{CH}_3)_2\text{CHCH}_2\text{OH}$	74	0.802 (20/4)	—	108.4	10%	1.394 (20)	4.2	0.66	138	85.5
Amyl alcohol (norm.)	$\text{CH}_3(\text{CH}_2)_4\text{OH}$	88	0.817 (20/4)	—	137	—	—	1.0	0.69	120	—
Isomyl alcohol	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{OH}$	88	0.810 (20/4)	—	131.4	2.5% miscible	1.406 (20)	—	0.66	125	91.6
Glycerol	$\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}$	62	1.265 (15)	11.5	197.5	—	—	—	0.63	113.3	113.3
Glycerol	$\text{HOCH}_2\text{CHOHCH}_2\text{OH}$	75	1.265 (15)	17	290	"	1.471 (20)	—	0.58	—	161.7
Hydrocarbons—											
Hexane	C_6H_{14}	86	0.660 (20/4)	-93	69	insoluble	1.373 (20)	75.0	0.50	79	57.6
Heptane	C_7H_{16}	100	0.681 (20/0)	-97	98	"	—	20.5	0.49	74	59.8
Octane	C_8H_{18}	114	0.704 (20/0)	-98	125.5	"	1.396 (20.6)	5.6	0.51	71	—
Decane	$\text{C}_{10}\text{H}_{22}$	142	0.730 (20)	-32	173	"	—	1.3	0.51	61	—
Benzene	C_6H_6	78	0.807 (20)	5.6	80.4	"	1.492 (28)	45.4	0.45	93	-4.1
Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	92	0.862 (0)	-92	110	"	1.491 (20)	13.0	0.42	84	+2.3

* M.P. = melting point.

† B.P. = Boiling point.

‡ Temperatures in brackets.

The figures in brackets indicate the temperature (°C.) of the liquid and of the water taken for comparison.

Alcohol is miscible in all proportions with water. The alcohol obtained by fermentation is always in a dilute condition, and requires somewhat elaborate treatment to separate it completely from the water. By fractional distillation it can readily be purified up to about 90 per cent. Very careful distillation with an effective fractionating column brings it up to 95.6 per cent., but beyond this point it is impossible to go by direct distillation, since a constant-boiling mixture of alcohol and water is obtained. Further removal of water may be effected by suitable dehydrating agents, but calcium chloride cannot be used, as it unites with alcohols, and sulphuric acid is inapplicable, as it destroys alcohol. Sodium hydroxide is not very effective. The drying agents generally used are quicklime, barium oxide, calcium carbide, metallic calcium, and magnesium amalgam.

It should also be mentioned that by careful fractional distillation of a mixture of alcohol, water, and benzene, a ternary mixture distils over at 64.85° and pure anhydrous alcohol can be prepared in this way.* The purest alcohol met with in commerce is usually about 99 per cent.

Anhydrous pure ethyl alcohol is known as "absolute" alcohol; it is somewhat hygroscopic when exposed to moist air. In some chemical reactions, complete absence of water is of great importance.

"Rectified spirit" contains 90 per cent. by volume or 85.68 per cent. by weight of ethyl alcohol, and has a specific gravity of 0.8337.

When alcohol is mixed with water, a contraction in volume occurs, and this must be taken into account when percentages by volume are being compared with percentages by weight. Thus, when 100 cu. cm. of alcohol are mixed with varying

* Young, *Journ. Chem. Soc.*, 1902, Vol. 81, 710.

quantities of water, the following contractions are observed.*

Water (cu. cm.) . .	5.17	31.05	93.15	186.3	248.4	372.6	621.0
Contraction (cu. cm.).	1.21	3.79	7.03	8.87	9.08	8.78	7.88

Proof Spirit. The term "proof spirit" is used to denote the standard strength recognized by the British Government as the basis for the assessment of duty on spirits. Until the last quarter of the eighteenth century, the methods of estimating the amount of alcohol in any mixture were very crude. One early way was to moisten gunpowder with the spirit under examination; if the powder ignited on the application of a light, the spirit was said to be "proof or over," but if the powder refused to burn, owing to the quantity of water in the spirit, the sample was said to be "under proof."

Between 1780 and 1800 several hydrometers were introduced, and the use of Sikes' hydrometer for testing the strength of spirits was legalized in 1816. Sikes called his standard strength "proof," and this standard was adopted for revenue purposes by the Spirits Act, 1818. In this Act proof spirit is defined as "spirit which, at a temperature of 51°F., weighs exactly twelve-thirteenths (12/13) of an equal measure of distilled water."

All British Government statistics relating to spirits are given in "proof gallons" (i.e. gallons at proof strength), with the single exception of industrial spirits, used in arts and manufactures, which are given in Imperial "bulk gallons."

Proof Spirit contains 49.3 per cent. by weight, or 57.1 per cent. by volume, of ethyl alcohol. *Industrial spirit* averages 64 per cent. over proof, corresponding to about 90.5 per cent. by weight, or 93.6 per cent. by volume, of alcohol.† The *British Pharmacopoeia* standard strength for the duty-paid spirit used by the drug trade is 58 per cent. over proof, corresponding to about 85.9 per cent. by weight, or 90 per cent. by volume, of alcohol. *Absolute alcohol*, i.e. pure ethyl alcohol, is 75.35 per cent. over proof.

* Holmes, *Journ. Chem. Soc.*, 1906, Vol. 89, 1775.

† Partly methyl alcohol, see Table IV, p. 26.

Relation between Proof Gallons and Bulk Gallons.

The equivalent proof gallons, i.e. gallons of spirit at proof strength, in any given bulk of spirit, depend upon the strength of the latter, over or under proof. If x be the number of degrees over or under proof, the percentage by volume of proof spirit in the alcohol under test is $(100 + x)$ in the case of over-proof (o.p.) spirit, and $(100 - x)$ in the case of under-proof (u.p.) spirit. In other words, if 100 be added to the figure representing strength over-proof, the sum is the volume of proof spirit making 100 volumes of spirit at the over-proof strength in question. Similarly, subtracting an under-proof strength from 100 gives the volume of proof spirit contained in 100 volumes of the alcohol in question. Thus, spirit at 25 o.p. is equivalent to 125 per cent. of its volume of proof spirit, whilst spirit at 25 u.p. contains 75 per cent. proof spirit.

To convert bulk-gallons to proof-gallons, or proof-gallons to bulk-gallons, or to determine the strength when the proof and bulk gallons are known, the following formulae may be used—

$$\begin{array}{l} \text{Percentage of proof spirit} = 100 + \text{strength over-proof} \\ \text{or} \quad 100 - \text{strength under-proof} \end{array} \left. \vphantom{\begin{array}{l} 100 + \text{strength over-proof} \\ 100 - \text{strength under-proof} \end{array}} \right\} (1)$$

as the case may be

$$\text{Proof gallons} = \frac{\text{Bulk gallons} \times \text{Percentage of proof spirit}}{100} \quad (2)$$

$$\text{Bulk gallons} = \frac{\text{Proof gallons} \times 100}{\text{Percentage of proof spirit}} \quad (3)$$

$$\begin{array}{l} \text{Strength of spirit} = 100 \left(\frac{\text{Proof gallons}}{\text{Bulk gallons}} - 1 \right) \text{over-proof} \\ \text{or} \quad 100 \left(1 - \frac{\text{Proof gallons}}{\text{Bulk gallons}} \right) \text{under-proof} \end{array} \left. \vphantom{\begin{array}{l} 100 \left(\frac{\text{Proof gallons}}{\text{Bulk gallons}} - 1 \right) \text{over-proof} \\ 100 \left(1 - \frac{\text{Proof gallons}}{\text{Bulk gallons}} \right) \text{under-proof} \end{array}} \right\} (4)$$

as the case may be.

Vapour Pressure. This is of importance, especially in connection with the question of the use of alcohol

in internal combustion engines. The following data are given by Merriman.*

V.p. (mm.)	50	100	150	200	250	300	350	400	450
Temp. (°C).	22.2	34.3	42.1	47.8	52.5	56.4	59.8	62.9	65.6
V.p. (mm.).	500	550	600	650	700	760	800	900	1000
Temp. (°C).	68.1	70.3	72.4	74.4	76.2	78.3	79.6	82.6	85.4

The heat of vaporization is given by Young.†

Temp. (°C.)	0°	10°	20°	30°	40°	50°	60°	70°	80°
Ht. of vap. cal. per grm.	220.9	221.2	220.6	220.1	218.7	216.0	213.4	209.9	206.4

The critical temperature is 243.6°C; at this point the density is 0.286.‡

Specific Heat. This is 0.618 at 20°C for the pure substance.§ For mixtures of alcohol and water the following data are given (22 to 99°C).—

Per cent. of alcohol by weight	20	40	60	80	100
Specific heat	1.044	0.992	0.908	0.803	0.660

Refraction. The refractive index for the β line of the hydrogen spectrum is 1.3667. The refraction of aqueous alcohols has been measured by Holmes|| and data at different temperatures are given by Dorochevsky and Dvorschantschik.* A maximum is observed when the alcohol is about 80 per cent. by weight.

Electrical Conductivity. This has been measured by Dorochevsky and Roschdestvensky.§§ The specific conductivity of pure alcohol at 15°C is given at 0.7×10^{-8} . Data are also given for mixtures of alcohol and water.

* *Journ. Chem. Soc.*, 1913, Vol. 103, 632.

† *Scient. Proc. Royal Dublin Soc.*, 1910, Vol 12, 441.

‡ Ramsay and Young, *Proc. Roy. Soc.*, 1885, Vol. 38, 329.

§ Dorochevsky and Rakowsky, *J. Russ. Chem. Soc.*, 1908, Vol. 40, 860.

|| *Journ. Chem. Soc.*, 1913, Vol. 103, 2165.

* *J. Russ. Chem. Soc.*, 1908, Vol. 40, 908.

§§ *Electro-Chemistry of Organic Compounds*, 1906, p. 60.

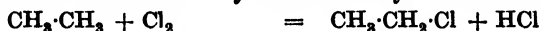
Viscosity. At 20°C the viscosity of pure alcohol is 1.200, compared with 1.005 for water. A mixture of equal parts by weight of alcohol and water has a viscosity of 2.87. The surface tension of alcohol at 20°C is 20.9 dynes per sq. cm.

Impurities. The main impurities in alcohol are higher alcohols (fusel oil), acetaldehyde, furfural, and volatile acids.

Alcohol as a Solvent. Next to water, alcohol is the most important solvent for industrial purposes. It dissolves inorganic salts only to a limited extent, but is a good solvent for organic materials such as resins, fatty acids, esters, soaps, essential oils, etc., and is used extensively in varnishes, and for crystallizing drugs and fine chemicals (Chapter VII). In admixture with ether, it dissolves the lower nitrocelluloses, and is largely used for this purpose in explosives and celluloid.

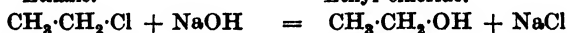
Chemical Equations representing Preparation of Ethyl Alcohol. The practical methods of preparation are dealt with in Chapters IV to VI. The following are mainly of chemical interest, and are included as illustrative of the constitution and chemical behaviour of the alcohols.

(a) The hydrocarbon ethane can be converted by means of chlorine to monochloroethane or ethyl chloride, and this can be further converted by alkali to ethyl alcohol—



Ethane.

Ethyl chloride.



Ethyl chloride.

Ethyl alcohol.

(b) Ethylene combines with sulphuric acid to give ethyl hydrogen sulphate, which on distillation with water yields ethyl alcohol (Chapter VI)—



Ethylene.

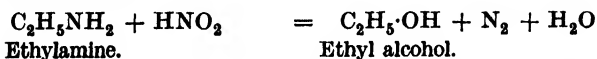
Ethyl hydrogen sulphate.



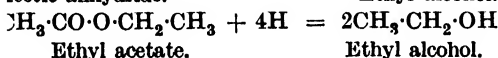
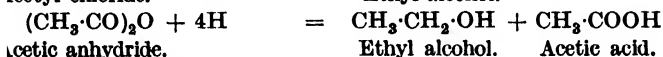
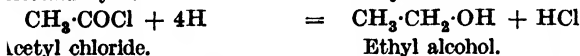
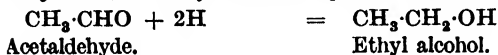
Ethyl hydrogen sulphate.

Ethyl alcohol.

(c) Ethylamine is converted to ethyl alcohol by the action of nitrous acid—

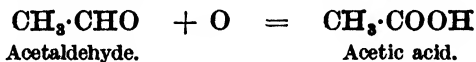


(d) Reduction of acetaldehyde, acetyl chloride, acetic anhydride, or ethyl acetate by zinc dust, etc.—

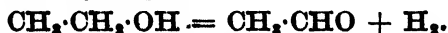


Chemical Reactions of Ethyl Alcohol. The following are the most important chemical reactions of ethyl alcohol, so far as they affect its industrial uses.

Oxidation. This converts ethyl alcohol first to acetaldehyde, and then to acetic acid—



A mixture of potassium dichromate and dilute sulphuric acid is generally used in the laboratory for the first stage. The use of permanganate or a greater excess of dichromate gives acetic acid. The direct oxidation to acetic acid is carried out on a large scale by bacteria in the manufacture of vinegar. In recent years, the catalytic conversion of alcohol to aldehyde and acetic acid has received attention. By passing alcohol vapour over copper or other catalysts at about 300°C ., it is converted directly to aldehyde and hydrogen—



This may then be oxidized to acetic acid by oxygen

in the presence of catalysts such as manganese acetate at ordinary temperature.

The electrolytic oxidation of alcohol to acetic acid has also been studied, but has not come into use as a practical method.

More vigorous oxidation of alcohol (with alkaline permanganate) gives oxalic, acetic, and carbonic acids.

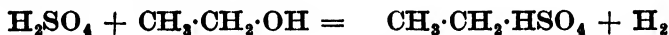
Conversion to Ether. This consists of a dehydration of ethyl alcohol—



Ethyl alcohol.

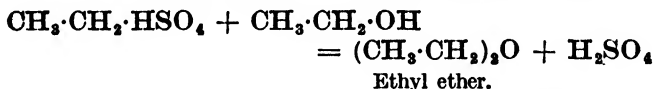
Ethyl ether.

It is effected in the laboratory by warming with sulphuric acid. Ethyl hydrogen sulphate is first formed, and this reacts further with formation of ether and sulphuric acid—



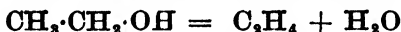
Ethyl alcohol.

Ethyl hydrogen sulphate.



Ethyl ether.

Conversion to Ethylene. This is brought about by a more vigorous dehydration of alcohol—



Ethyl alcohol.

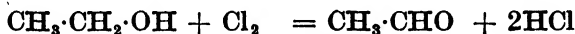
Ethylene.

It was formerly carried out by means of hot concentrated sulphuric acid, which forms ethyl hydrogen sulphate as an intermediate product. It is now more usually effected by passing the alcohol vapour over hot phosphoric acid. The same reaction takes place, together with the formation of a certain amount of aldehyde, when the alcohol vapour is passed over solid catalysts at a high temperature. Kaolin, and the oxides of aluminium, tungsten, thorium, etc., can be used. In the case of some catalysts, methane, hydrogen and carbon monoxide are formed.

These catalytic reactions are of importance in

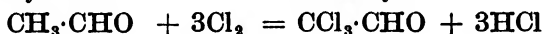
considering the use of alcohol for internal combustion engines.

Action of Chlorine. This gives chloral hydrate, chloral alcoholate, and trichloro-acetal. Chloroform may be prepared from alcohol and bleaching powder. The reaction is believed to take place as follows—

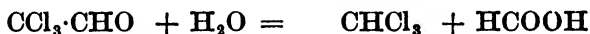


Ethyl alcohol.

Acetaldehyde.



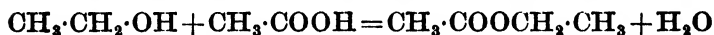
Chloral.



Chloroform.

Formic acid.

Formation of Esters. When alcohol is warmed with an organic acid in presence of concentrated sulphuric acid, esters are formed as in the equation—



Ethyl alcohol.

Acetic acid.

Ethyl acetate.

These esterifications form the basis of numerous industrial applications.

Analytical Methods. Ethyl alcohol may be identified by the following reactions—

(a) Iodine and sodium carbonate solution give, on warming, the characteristic odour of iodoform. Other substances also, however, give this reaction.

(b) Warming with dilute sulphuric acid and potassium dichromate gives a smell of acetaldehyde.

(c) On warming with concentrated sulphuric acid and an organic acid, such as acetic or salicylic, the alcohol is converted to an ester. It is not, however, possible to distinguish with certainty between the different alcohols by this test.

(d) Benzoyl chloride reacts with alcohol to form ethyl benzoate, which can be detected by its smell after removing the excess of benzoyl chloride with caustic soda. Para-nitrobenzoyl-chloride similarly yields ethyl para-nitrobenzoate which melts at 57°C.

(e) When warmed with phthalic anhydride, ethyl alcohol gives ethyl phthalate. When the sodium salt of this is heated with para-nitrobenzyl bromide, a mixed ester of melting point 80° is obtained.

Various other reactions are used for the identification of this and other alcohols.*

Alcohol may be estimated quantitatively by conversion to iodoform; this is then boiled with potassium hydroxide solution, and the iodine is estimated with silver nitrate. An alternative method is to oxidize the alcohol to carbon dioxide with alkaline permanganate and to determine the excess of permanganate.

Small quantities of water in alcohol may be estimated by adding petrol and finding the critical solution temperature.† A similar method has been used with α -bromonaphthalene.‡ A useful method for the detection of small quantities of water by means of aluminium ethoxide has been given by Heule.§ Further tests for traces of water depend upon the colour imparted to anhydrous copper sulphate, and the fact that anhydrous alcohol dissolves barium oxide and the solution gradually becomes yellow.

* See Simmonds' *Alcohol*, p. 200.

† Nussbaum *J. Pharm. Chim.*, 1917, Vol. 15, 230.

‡ Jones and Lapworth, *Journ. Chem. Soc.*, 1914, Vol. 105, 1086.

§ *Ber. deutsch Chem. Gesell.*, 1920, Vol. 53, 719.

CHAPTER III

EXCISE REGULATIONS AND DENATURING

For many centuries alcohol was known only as a stimulating beverage. As such, it was very naturally considered a fit subject for taxation when revenue was required in various countries. In the early part of last century other uses of alcohol gradually came into existence. It was found to be convenient for heating purposes on a small scale; and it was found to have useful solvent properties, rendering it of great value for making varnishes and polishes, and so on.

Denaturing and Denaturants. In order that such applications of alcohol might be encouraged, it was necessary that a remission of duty should be made, but at the same time it was necessary to distinguish between alcohol for drinking purposes and that used for other purposes. It was in Great Britain that this requirement was first met, in 1855, by adding nauseous substances to alcohol to render it undrinkable, and permitting such alcohol to be used free of duty for other purposes. This process is called "denaturing," and the materials used for mixing with the alcohol are called "denaturants." The admixture chosen was commercial wood alcohol, which is a mixture of liquids very unpleasant in taste. In course of time other countries made similar enactments, and the use of denatured alcohol or "methylated spirit" for industrial purposes became general.*

* For detailed historical accounts see Tweedy's *Industrial Alcohol*; Simmonds' *Alcohol*; Tunison, *Journ. Frankl. Inst.*, 1920, Vol. 190, 373.

At first, duty-free methylated spirit was permitted only for manufacturing purposes. In 1861, it was permitted for general sale in limited quantities, but if used on a large scale it was subject to Excise supervision. In 1891, a further type of denaturation was introduced ; the alcohol containing 10 per cent. of wood spirit was permitted only for manufacturing purposes, where some degree of control could be exercised. For domestic and general use the further addition of 0.375 per cent. of mineral naphtha was instituted. This constitutes what is known as "mineralized" methylated spirit.

In 1906, a relaxation was made in the amount of wood naphtha in industrial methylated spirit. The wood naphtha added materially to the expense of the alcohol, and was therefore reduced from 10 per cent. to 5 per cent. At the same time, a rebate was made to manufacturers to compensate for the expense due to Excise supervision. The amount of this rebate is 3d. per proof gallon, equal to nearly 5d. per gallon of 95 per cent. alcohol.

Since the wood naphtha interferes occasionally with the use of the alcohol in manufactures and contaminates the products, special denaturants are allowed in some cases. In these, a denaturant is chosen with special reference to the manufacturing operation in question, so that whilst still making the alcohol unpotable, it may not introduce harmful contamination.

Up to 1906, mineralized spirit was not permitted to be sold in quantities of more than one gallon at a time, but from this time onward the limit was raised to four gallons.

Temporary modifications were made during the war to conserve the supplies of wood spirit, but these need not be specified here.*

The present regulations demand that mineralized

* See Simmonds' *Alcohol*, p. 297, for details.

spirit shall contain one-tenth of its volume of wood naphtha to which 0·375 per cent. of mineral naphtha has been added. Industrial methylated spirit contains one-twentieth of its volume of wood naphtha and no mineral naphtha. Since June, 1918, mineralized methylated spirit has been tinted with methyl violet.

Rates of Duty. As is well known, these have undergone a great increase in recent times. In 1918, the Excise duty on plain spirits warehoused for three years or more was 30s. per proof gallon. This was subject to an increase of 1s. for spirit warehoused between two and three years, and 1s. 6d. for immature spirit warehoused less than two years. The Customs duties were 5d. per proof gallon more than the above. The above 30s. rate was increased to 50s. in 1919, and to 72s. 6d. in 1920. No change was made in 1921.

Consumption of Methylated Spirits. The consumption of methylated spirits in the United Kingdom for the years 1909 to 1914 was as shown in Table II.

TABLE II.—CONSUMPTION OF METHYLATED SPIRITS IN THE UNITED KINGDOM, IN MILLIONS OF IMPERIAL GALLONS.

Year ended 31st March.	Industrial Methylated Spirit.	Mineralized Methylated Spirit.	Total.
1909	2·54	1·63	4·17
1910	2·40	1·56	3·96
1911	2·88	1·69	4·57
1912	3·09	1·72	4·81
1913	2·85	1·58	4·43
1914	3·25	1·75	5·00

In Germany the total quantity for 1912 was 34½ million gallons ; this was made up as in Table III.

TABLE III.—CONSUMPTION OF TAX-FREE ALCOHOL
IN GERMANY (1912).

	Imp. Galls. of pure Alcohol.
<i>Completely denatured—</i>	
With general denaturing formula	25,813,000
With benzol mixture	1,021,000
<i>Incompletely denatured—</i>	
With 5 litres wood alcohol per hectolitre .	352,000
With 0.5 litre turpentine per hectolitre .	31,000
With other denaturants.	6,763,000
<i>Without denaturation—</i>	
For hospitals etc.	120,000
For public scientific institutions	45,000
For military technical institutions . . .	222,000
For gunpowder and fulminate factories .	264,000

Alcohol in the United States. In the United States, a tax on distilled spirits was apparently first imposed in 1791. This was repealed in 1802, but again imposed in 1813. In 1817 the law was again repealed ; no tax was imposed until the time of the Civil War, when a tax of 20 cents per gallon was levied. This was increased in 1868 to 50 cents, in 1872 to 70 cents, in 1875 to 90 cents, in 1894 to \$1.10, and in 1917 to \$3.20 per proof gallon for beverage spirits and \$2.20 for non-beverage spirits. Certain relaxations were permitted in the case of alcohol for scientific and research purposes. The recent National Prohibition Act had as one of its purposes to insure an ample supply of alcohol for lawful industries and to promote its use in scientific research, whilst prohibiting intoxicating beverages. It provides for the supply of duty-free alcohol to Universities Hospitals etc. Many different

formulae are in use for the denaturing of alcohol. Doran* states that these number thirty-five.

Alcohol in France. In France denatured alcohol has been permitted since 1872, when a tax amounting to about 1s. 5d. per gallon was fixed by law. A slight increase was made in 1895 (about $\frac{1}{2}$ d. per gallon) to cover the cost of supervision. In 1901 a bounty was granted to manufacturers using denatured alcohol to encourage its use. This amounted at first to about 2 $\frac{1}{2}$ d. per gallon, and was raised subsequently to about 4d. per gallon. The cost of the bounty was covered by a tax on all distillers of alcohol, which varied from year to year (in 1910, 2s. 7d.; in 1911, 2s. 3 $\frac{1}{2}$ d.) The manufacturer of denatured alcohol pays a tax of about $\frac{1}{2}$ d. per gallon.

Requirements of a Denaturant. The primary requirement is that the denaturant shall mix readily with the alcohol and render it unpotable. Other requirements are—

(1) That it shall be practically impossible to remove the denaturant, by distillation or otherwise, so as to render the alcohol potable.

(2) That the cost of the denaturant shall not add too much to the cost of the alcohol.

(3) For manufacturing purposes, that the denaturant shall not unduly contaminate the products or increase the difficulty of purifying them.

(4) That, whilst rendering the alcohol unpotable, the denaturant shall not be unduly obnoxious in smell, nor highly poisonous.

(5) That the denaturant shall be so effective that the addition of a small percentage shall suffice.

(6) That it shall be readily detectable in small quantities by chemical tests.

It is recognized that in skilled hands almost any denaturant could be removed from alcohol, but if the separation is difficult and expensive the object of the denaturant may be considered to have been served. Heavy penalties act as a deterrent to any

such evasion of the alcohol duties. For power alcohol a further desideratum is that the denaturant and its combustion-products shall not unduly corrode metals.

Materials used as Denaturants. The main substance used for denaturing is wood naphtha, which consists of an impure methyl alcohol. Typical compositions of mineralized and industrial methylated spirit at 62° over proof, as given by Simmonds,* are reproduced in Table IV. The figures are given in parts per cent. by volume, and add up to more than 100 on account of the contraction on mixing.

TABLE IV.—COMPOSITION (PERCENTAGE VOLUME) OF MINERALIZED AND INDUSTRIAL METHYLATED SPIRIT.

	Mineralized methylated spirit.	Industrial methylated spirit.
Ethyl alcohol	83.05	87.92
Methyl alcohol	7.73	3.87
Ketones (as acetone) . .	1.02	0.51
Esters (as methyl acetate) .	0.13	0.06
Unsaturated compounds (as allyl alcohol)	0.08	0.04
Basic compounds (as pyridine)	0.02	0.01
Mineral naphtha	0.38	0.00
Water	9.21	9.21
	101.62	101.62

The reasons why wood naphtha stands out as an excellent denaturant are that it mixes completely with ethyl alcohol, and is very difficult to separate by any means. It is, moreover, easy to detect and

* *Alcohol*, pp. 293, 296.

identify in small quantities, and thus methylated spirit can be readily distinguished from pure ethyl alcohol. The impurities in the wood naphtha (pyridine, etc.) make the methylated spirit undrinkable, except to the most depraved tastes.

The properties of the ingredients mentioned above are given in Table V. Due to the insolubility of mineral naphtha in water, methylated spirit becomes turbid when diluted with water.

TABLE V.—PROPERTIES OF INGREDIENTS OF METHYLATED SPIRIT.

	Formula.	Sp. gr. (at °C.).	Boiling Point °C.	Solubility in Alcohol.	Solubility in Water.
Ethyl alcohol	$\text{CH}_3\cdot\text{CH}_2\text{OH}$	0.789 (20°)	78.3	miscible	miscible
Methyl alcohol	$\text{CH}_3\cdot\text{OH}$	0.796 (20°)	66°	"	"
Acetone	$\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3$	0.792 (20°)	56°	"	"
Methyl acetate	$\text{CH}_3\cdot\text{COOCH}_3$	0.957 (0°)	57.5°	"	partial
Allyl alcohol	$\text{CH}_3\cdot\text{CH}\cdot\text{CH}_2\text{OH}$	0.858 (15°)	97°	"	miscible
Pyridine	$\text{C}_5\text{H}_5\text{N}$	0.986 (0°)	116.7°	"	"
Mineral naphtha	—	0.8 to 0.83	—	"	insoluble
Water	H_2O	1.00	100°	"	miscible

Specially Denatured Alcohol. In the case of specially denatured alcohol a wider range of denaturants is employed, but it is a primary essential that the unsuitability of methylated spirit must be proved to the satisfaction of the Commissioners of Customs and Excise, and steps must be taken for the security of the Revenue. The chief industries which employ specially denatured alcohol are those making various fine chemicals, dyes, explosives, and celluloid products. The total quantity of this special alcohol used in the year 1913–14 was about 750,000 proof gallons.

The special denaturants which have been most frequently used are benzene, aniline, bone-oil,

pyridine, turpentine, and petrol. Where possible, a certain proportion of wood spirit is still added for identification purposes.

Denaturants for Power-Alcohol. Since the question of "power-alcohol" came to the fore, there has been a search for new denaturants which shall be more suitable for internal combustion engines. The Committee on Power Alcohol recommended in 1919 (Cmd. 218) that every effort should be made by research and practical trial to provide a denaturant or alternative denaturants—e.g. formaldehyde, pyridine, and tobacco oil—the employment of which would be effective in the smallest possible quantities, and at the lowest possible cost per gallon.

Russia, Sweden and other countries have, at different times, offered prizes for the discovery of a suitable denaturant.

The Empire Motor Fuels Committee in its report of February, 1921, indicated re-distilled bone oil, light caoutchoucine and shale oil products as the most suitable denaturants but others are also under investigation. Probably no one substance will meet all the requirements; in this case mixtures will have to be used.

Experiments are now being made at the British Government Laboratory on a denaturant recommended by the Committee on Power Alcohol in Australia, namely, the distillate obtained from coal tar oil at 170° to 230°C.*

Cost of Denaturing The cost has been variously estimated. The chief item is the high cost of wood naphtha, the principal denaturant. It is stated in the Report of the Committee on Power Alcohol, 1919 (Cmd. 218), that the denaturing process may increase the cost by 6d. per gallon, and this Committee recommends a reduction in the proportion of wood

* Report by Sir J. J. Dobbie for the Alcohol Motor Fuel Committee, *Journ. Soc. Chem. Ind.*, 1920, Vol. 39, 86R.

naphtha and the substitution of petrol, benzol, etc., with a little methyl violet to colour the spirit.

Major-General Sir John Fowler* states that, owing to the decreased demand for charcoal in this country, the supply of wood naphtha has also decreased, and the cost of this has increased from 3s. to 12s. or 15s. per gallon. He estimates that the denaturing costs probably 2s. per gallon of methylated spirit.

The following data were given by Sir J. J. Dobbie in a report drawn up for the Alcohol Motor Fuel Committee.†

TABLE VI.—INCREASE IN COST OF DENATURED SPIRIT DUE TO USE OF WOOD NAPHTHA AS DENATURANT.

	1906.	1907.	1909.	1914.	1919.
1. <i>Mineralized Methylated Spirit.</i>	s. d.	s. d.	s. d.	s. d.	s. d.
Selling price of alcohol per bulk gallon 61 o.p. (91% alcohol by volume)	1 4	1 6½	1 10½	2 1½	7 2½
Average price of wood naphtha per bulk gallon	Mean 1906 to 1914, 2s. 8d.				11 6
Increase in cost of denatured spirit due to admixture with 10% wood naphtha	1-60d.	1-36d.	0-96d.	0-64d.	5-16d.
2. <i>Industrial Methylated Spirit.</i>					
Selling price of alcohol per bulk gallon 66 o.p. (95% alcohol, by volume), not deducting drawback	1 4½	1 7	1 11½	2 2½	7 5½
Increase in cost of denatured spirit due to admixture with 5% wood naphtha	0-77d.	0-90d.	0-68d.	0-52d.	2-66d.

Analysis of Denatured Spirits. The following tests are usually made—

(1) *Alcoholic strength* : For this, the hydrometer test is usually sufficient.

(2) *Methyl alcohol* : This is determined by oxidation with permanganate and colorimetric estimation of the formaldehyde with Schiff's reagent.

* *Times Trade Supplement*, 3rd July, 1920, p. 436.

† *Journ. Soc. Chem. Ind.*, 1920, Vol. 39, 86R.

(3) *Acetone* : Sodium hydroxide and iodine are added to convert the acetone to iodoform and the excess of iodine is titrated. A control test is made with the same reagents on pure alcohol of the same strength, and the result is deducted from that of the sample.*

(4) *Mineral naphtha* : This is precipitated by water, and the opalescence is compared with that of a standard sample.

(5) *Esters* : The spirit is first neutralized with sodium hydroxide solution ; excess of sodium hydroxide is then added and the solution is heated on a steam bath to saponify the esters. The excess of alkali is titrated with acid.

(6) *Unsaturated compounds* : The spirit is added to a standard bromine solution until this is just decolorized.

Numerous tests have been devised for the detection and estimation of minute traces of methyl alcohol, mostly depending on the oxidation of the alcohol to formaldehyde or formic acid. A critical study of 58 tests was made by Gettler.† A useful review, up to 1905, was made by Scudder,‡ and details of the most important tests are given by Simmonds.§ In order to concentrate the methyl alcohol in the form of formaldehyde, the sample (100 cu. cm.) is neutralized with sodium carbonate, using phenol phthalein as indicator, and distilled slowly until 50 cu. cm. have been collected. A mixture of 100 cu. cm. of 10 per cent. sulphuric acid and 6 grms. of potassium bichromate is allowed to stand for ten minutes, and 30 cu. cm. of the above distillate are added to it. The solution is distilled slowly. The first 30 cu. cm. contain most of the acetaldehyde, but the following 60 cu. cm. contain most of the formaldehyde, and are used for the various colour-reactions.

Excise Regulations and their bearing on Power Alcohol. A good deal of criticism has been levelled against the present regulations in respect to their

* Simmonds' *Alcohol*, p. 294.

† *Journ. Biol. Chem.*, 1920, Vol. 42, 311.

‡ *J. Amer. Chem. Soc.*, 1905, Vol. 27, 892.

§ *Alcohol*, p. 173.

bearing on the production and sale of cheap alcohol for power purposes (Chapter VIII). Recent developments make it a matter of urgency that no artificial restrictions shall hamper Great Britain in its competition with other countries in this respect.

The main restrictions have been set forth by Mr. Tweedy*, Major-Gen. Sir John Fowler†, Viscount Elveden and Mr. Sinkinson,‡ and others. The general criticism is that the Customs and Excise regulations are based on an Act of 1880 framed at a time when no question of power-alcohol existed, and that these regulations as applied to present-day conditions are irksome and form a hindrance to private enterprise. Detailed rules are laid down for the production of alcohol, entailing unnecessary expense in premises and plant, and precluding the use of the most modern and efficient modes of production. It is pointed out (Tweedy) that the most productive method of fermentation is debarred, because the wort would be too thick to allow of the use of the saccharometer prescribed by the Act of 1880. The plant and buildings have to be several times larger than they need be, owing to the absolute prohibition of brewing and distilling simultaneously. The distillery must be shut down altogether from 11 p.m. on Saturday until 1 a.m. on Monday, thus precluding continuous operation which would bring about increased efficiency and economy. By-products must not be worked; thus it is forbidden to refine sugar or to make starch. Plant is stereotyped, and there is no encouragement to introduce improvements in method or in apparatus. Transport by tank is forbidden, and no distillery is permitted to be more than a quarter of a mile from a market town, whereas it would frequently be better to situate the distillery near to the raw materials.

* *Industrial Alcohol*.

† *Times Trade Supplement*, 3rd July, 1920, p. 436.

‡ "*Reuma*" *Journal* 1920 Vol 7 pp 80 172

Sinkinson points out the advantage which would accrue if the volumetric mixings of alcohol and denaturant could be permitted to be made in any suitable storage vessel, even though such vessel contained power-alcohol previously denatured, provided that no supplies were drawn until the new mixing was completed. He also urges the importance of permitting fermentation and distillation in the same building, and of continuous stills, thus permitting of the use of the fermenting mould Mucor Boulard No. 5, without any modifications. He states further that the adoption of the alcoholometer or other direct means of determining the alcohol would allow of improvements which would treble or quadruple the output. Obviously, any facilities which would permit of increased capacity would reduce the price by decreasing the maintenance charges.

A further subject of criticism is that since internal combustion engines are not regarded as an art or industry, they have not the privilege of using "industrial methylated spirit," but must use "mineralized" spirit, and purchases are restricted to 4 gallons at one time. The retailer is also limited to a certain stock. The larger proportion of wood naphtha in mineralized spirit is stated to cause corrosion of the engines. The wood naphtha has to be imported, for the most part, and adds considerably to the cost of the spirit. Denaturing carried out abroad is not recognized by our authorities and imported methylated spirit must be again denatured to satisfy the regulations. Alcohol imported into bond for methylation is subject to "differential customs duty," that is, to the difference between the customs duty on imported alcohol and the excise duty on its manufacture in this country. The full rate of duty on alcohol such as would be used for power purposes imported from countries outside the Empire is about 4s. 9d., and the preferential

rate on alcohol from within the Empire about 8½d. per bulk gallon. Major-Gen. Sir John Fowler contends that with this charge and the cost of denaturing, imported alcohol is handicapped out of possible competition with petrol in this country.

The Committee on Power Alcohol has made recommendations to meet some of these points (Cmd. 218). It suggests a relaxation of the regulations to permit the use of any suitable tank for the volumetric mixings, notwithstanding the fact that such vessel may still contain power-alcohol previously denatured. If power-alcohol is satisfactorily denatured before importation, the Committee considers it superfluous to impose the usual bonded-warehouse regulations upon these who store and handle it after landing. It recommends that tank wagons should be allowed for transport; and that power-alcohol produced in the United Kingdom should be exempt from motor-spirit tax (excise). The relaxations recommended are subject to the condition that the user gives bond, and that precautions are taken to avoid any misuse of the alcohol. Thus heavier penalties are proposed in case of any evasion of the duties.

The question is largely one of a suitable denaturant. If an ideal denaturant could be found, much greater freedom would obviously be possible in other directions. The above Committee lays stress on the importance of finding better denaturants. It recommends a substantial reduction in the proportion of wood-naphtha, the difference being made up by benzol, etc., with a small quantity of colouring matter.

An Alcohol Excise Restrictions Sub-committee has also been appointed by the Empire Motor Fuels Committee to investigate the Excise regulations.

Certain concessions were indicated in 10 and 11 Geo. 5, Ch. 18, Sec. 11, in the direction of bringing power alcohol more into line with industrial spirit.

Table VII summarizes conveniently the denaturants in, and the limitations upon, the use of the types of alcohol now (1921) in use in this country.

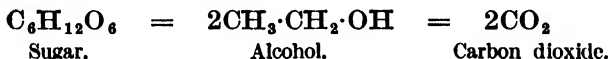
TABLE VII.—SUMMARY OF THE TYPES OF ALCOHOL IN USE IN GREAT BRITAIN AND IRELAND.

Designation.	Denaturants.	Limitations of use, when Duty-free.
Plain spirit.	None.	Small quantities for scientific and research purposes.
Industrial methylated spirit.	5 per cent. wood naphtha.	Manufacturers only; not permitted to be sold by retailers. Minimum quantity obtainable at once, 5 gallons.
Mineralized methylated spirit.	10 per cent. wood naphtha and 0·375 per cent. mineral naphtha.	May be sold by licensed retailers in quantities not exceeding 4 gallons for general use.
Specially denatured alcohol.	Special denaturants.	By special permission, in manufactures where ordinary methylated spirit would be detrimental; subject to certain regulations laid down by the Commissioners of Customs and Excise.

CHAPTER IV

PRODUCTION OF ALCOHOL BY FERMENTATION AND DISTILLATION

Fermentation. By far the most important process at present for the production of alcohol is the fermentation of sugars, especially hexoses, by yeast. The conversion of sugar to alcohol takes place according to the equation—



It has been known for some 300 years that a ferment is necessary (van Helmont). Early in the nineteenth century it was ascertained that the fermentation was connected with the life-process of the yeast cells. The nature of fermentation formed the subject of much discussion, but very little progress was made until Pasteur commenced his valuable studies on the fermentation process. He showed that, apart from alcohol and carbon dioxide, succinic acid and glycerine are formed. He showed also that each type of fermentation requires its own special form of micro-organism, and that fermentation is a consequence of a continued and progressive life-process. Further, he showed that the yeast requires nutriment in the form of nitrogenous and other organic substances and inorganic salts.

In 1858, Traube had explained that fermentation was due, not to the yeast-cells themselves but to certain substances which were secreted in these cells. This received but little credence at the time, but was confirmed towards the end of the century by Buchner,* who found that by pressing out the

* *Ber. deutsch. Chem. Gesell.*, 1897, Vol. 30, p. 117.

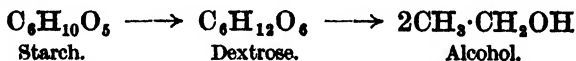
yeast-cells a liquid was obtained which was capable of bringing about fermentation by virtue of an enzyme "Zymase" which it contained.

With the development of bacteriology and the use of the microscope great progress has been made in the isolation of the different organisms. Meanwhile, the mechanical methods have undergone great improvements, particularly with reference to distillation and purification plant.

The process can only be dealt with briefly in the present chapter, but more detail can be obtained in numerous text-books (see Bibliography, p. 107).

Raw Materials. The raw materials which serve as a basis for the preparation of alcohol by fermentation are vegetable substances which contain either sugar, or other carbohydrates which can be converted to sugar. Of these latter, starch is by far the most important, and this forms the chief ingredient of potatoes, rice, maize, corn and many other vegetable products. In the United Kingdom, grain and molasses are generally used; in Germany, potatoes; in France, beet, maize and molasses; in Russia, potatoes and grain; and in the United States, grain, molasses, and potatoes.

Yield of Alcohol. On the basis of the conversion of starch to alcohol, as represented in outline as follows—



it is calculated that 100 parts of starch should yield fifty-six parts by weight of alcohol. In practice the yield is about 85 to 90 per cent. of the theoretical.

The treatment of the various starchy materials follows the same general lines. The starch has first to be converted to sugar, and this is fermented to alcohol. The conversion to sugar is generally effected by malt (obtained from barley), which contains an

enzyme "diastase" capable of converting the starch to sugar. Where the raw material contains sugar, this treatment is unnecessary. The sugar is then fermented by yeast. Finally, the alcohol has to be isolated from the mixture and purified. The following is a very brief outline of the method used for potatoes; the details differ at different places.

Preparation of Alcohol from Potatoes. The potatoes are heated in a closed vessel with steam at $2\frac{1}{2}$ to 3 atmospheres pressure. After heating, the steam pressure is suddenly released, and this converts the potatoes to a uniform mash, which contains the starch in the form of paste, and is thus suitable for the action of the diastase of the malt. The conversion of the starch to sugar is carried out in vats provided with agitators, by means of malt at about 60°C . The mash is then cooled as rapidly as possible to between 15° and 18°C , in order to avoid any fermentation due to foreign micro-organisms which act differently from the yeast. The liquor may then be separated from the solid matter. A pure yeast is then added to the sweet mash at 20°C , the vat being fitted with coolers, so that the temperature may not exceed from 27.5° to 30°C during the main fermentation. In the after-fermentation (consisting of a fermentation of the dextrin which is formed) the temperature is kept below 26 to 29°C . Finally, the alcohol formed is distilled from the fermented mash, and at the same time rectified in a continuous still. The flow sheet in Fig. 1 is adapted from Ost* to show the operations in the conversion of potatoes to alcohol.

Amylo-process. In the manufacture of alcohol for spirit, especially starting from maize, moulds such as aspergillaceae and mucors have come into use to

* *Lehrbuch der Chem. Tech.* 1914, p. 528.

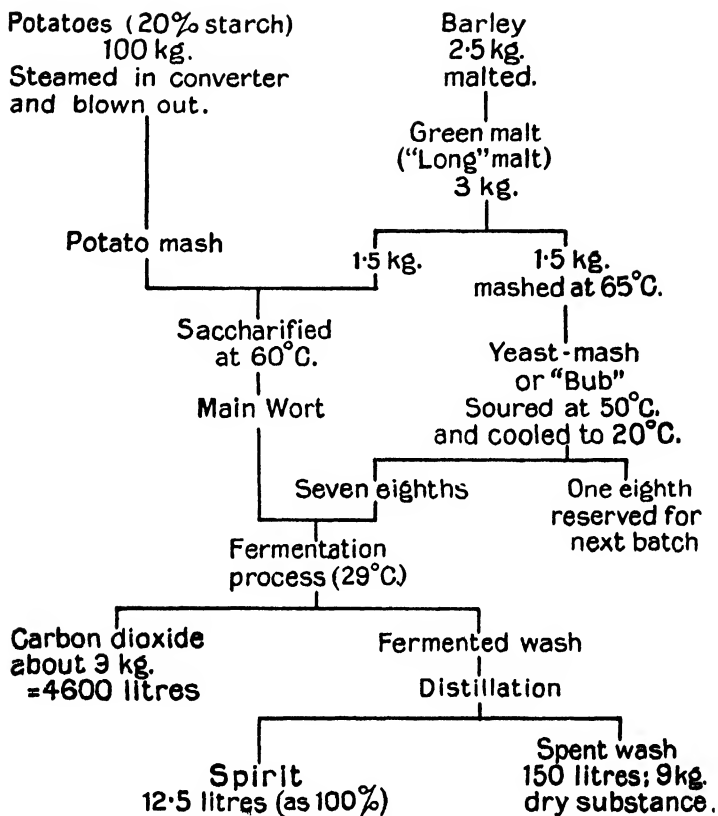


FIG. 1.—FLOW SHEET REPRESENTING CONVERSION OF POTATOES TO ALCOHOL.

some extent. These have the advantage that they effect both the saccharification and the fermentation. Moreover, a great saving is effected, as a small quantity of mould takes the place of a much larger quantity of malt. Such moulds had been used for many centuries in China for the production of alcohol from rice. The first large scale experiments were made in 1898 in the distillery of M. Auguste Collette, near Lille. The process gives good yields, as unfermentable dextrins are not formed during saccharification, and it is possible by using a sterilized mash to avoid side-fermentations very completely, but some difficulty has been encountered in the contamination of the vats by other organisms. Yields up to 97.5 per cent. of the theoretical have been claimed. The process is especially suitable for hot climates, where difficulty is experienced in the preparation of malt. The moulds now generally used are *Rhizopus Delemar* and *Mucor Boulard*. The process takes about four days, after which the spirit can be distilled off directly. Sometimes this process is used in conjunction with the malt process, some malt being added to assist in the conversion of the starch to sugar, and a suitable yeast being added later to accelerate the fermentation to alcohol. An account of the method is given by Grove.* Some 6,000,000 hectolitres of alcohol have been made in this way in France, Spain, Italy, Germany, and America. The difficulty of introducing it into this country on account of excise restrictions has been mentioned in Chapter III. The use of starch-liquefying enzymes forms another improvement in fermentation methods (*cf.* Cantor Lectures, 1920).

By-products of the Fermentation. The most important of these are propyl alcohol, isobutyl alcohol, isoamyl alcohol, glycerine, succinic acid, acetic acid, butyric acid and other fatty acids,

* *J. Inst. Brewing*, 1914, Vol. 20, p. 248.

lactic acid, acetaldehyde, acetal, esters, and mannite. Furfurol, basic and terpenic compounds are also present as products of the decomposition of woody material.

The conditions under which the proportion of glycerine can be increased have received considerable study, especially in Germany during the war, on account of the importance of glycerine for explosives. It was already known that the glycerine could be increased to 7 or 8 per cent. but, by special methods of fermentation, the Germans increased the proportion of glycerine very greatly, even to the extent of 36 per cent. on the laboratory scale. The method was utilized on a large scale, and gave yields of 20 to 25 per cent. of the theoretical.*

In general, however, it is desirable to remove the by-products as far as possible, and this is effected by fractional distillation, as described below.

Distillation. From the above outline of the fermentation process, it is seen that the product is a mixture containing, in addition to the alcohol formed, a large proportion of water, smaller quantities of fusel oil and other by-products, and a residual solid mass of husks, etc. The alcohol is separated from these by a distillation process.

Under ordinary circumstances, where the alcohol is required in a dilute condition for drinking purposes, no attempt is made to separate it entirely from the esters and higher alcohols, as these contribute to the flavour of the product. In this case a very simple form of still suffices, but where the alcohol has to be concentrated and freed from impurities much more elaborate stills have to be used.

Pot Stills. These are the simplest form of stills in use for the distillation of alcohol. The apparatus (Fig. 2) requires no explanation. In some cases it

* Stettbacher, Z. Schiess. Spreng., 1920, Vol. 15, p. 165.

is elaborated by a simple form of fractionating column. The stills may be heated, either by direct firing or by a steam jacket or coil. In the former case it is desirable to keep the contents of the still stirred—in order that the sediment may not become burnt.

The first distillate is very impure, and must be redistilled to render it fit for drinking purposes; it still contains far too much water for other uses.

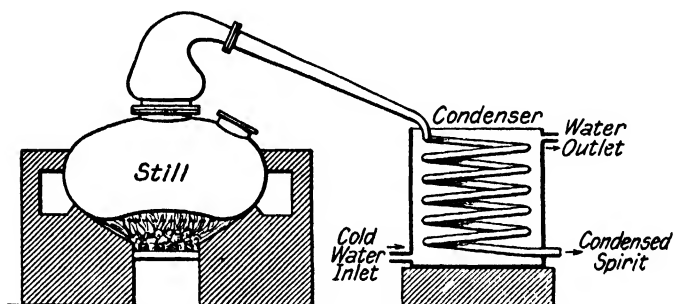


FIG. 2.—SIMPLE POT STILL.

Fig. 3 shows a somewhat more elaborate still for the rectification of alcohol.

The heating pan 1 is fitted with a steam coil in which the pressure is controlled by the regulator 11. The spirit vapour passes through the pipe 2 into the rectifying column 3 which contains forty to fifty plates. Thence it passes through the pipe 5 to the condenser 4 which is generally of the tubular type. The cooling water is so regulated that a considerable portion of the spirit is condensed and returned to the rectifying column. The uncondensed vapour passes through 6 to the cooler 7 and the liquid flows to the outlet taps 10.

The cooling water flows from the tank 14 through 13 and pipe 9, through the cooler 7, thence by pipe 8 to the condenser 4 and finally to 12, from which it passes away through an overflow pipe.

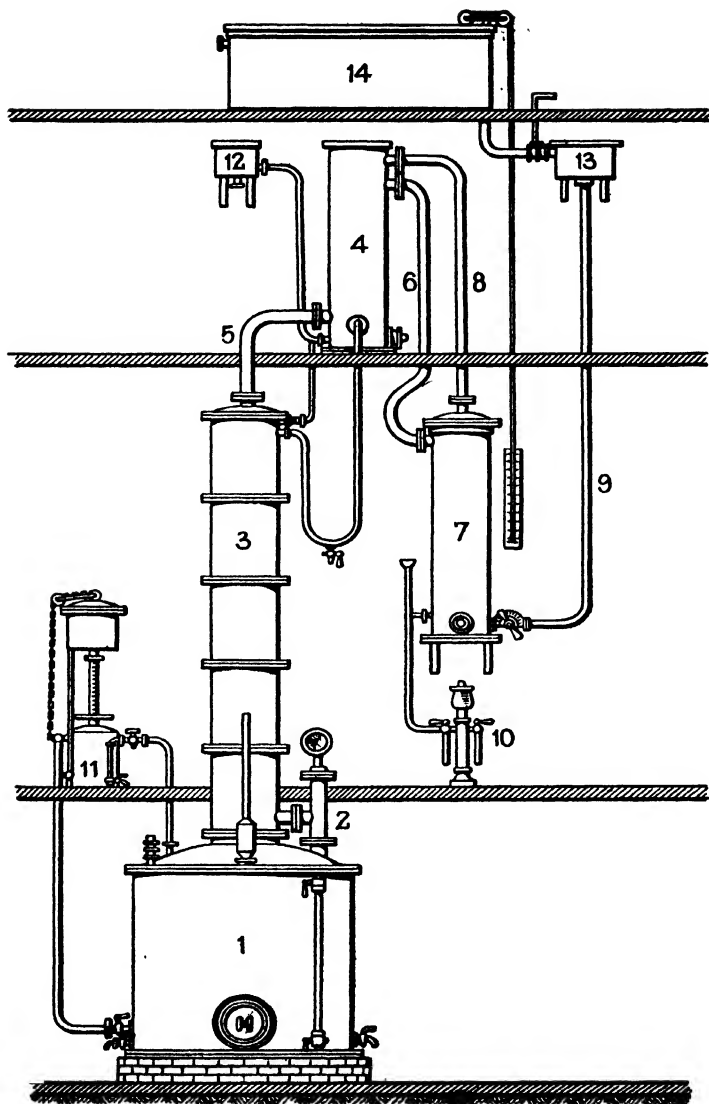


FIG. 3.—DISCONTINUOUS RECTIFYING STILL.

- | | |
|-----------------------|--------------------------------|
| 1. Heating pan. | 10. Outlet taps. |
| 3. Rectifying column. | 11. Steam pressure regulator. |
| 4. Condenser. | 12. Cooling water outlet. |
| 7. Cooler. | 14. Cooling water supply tank. |

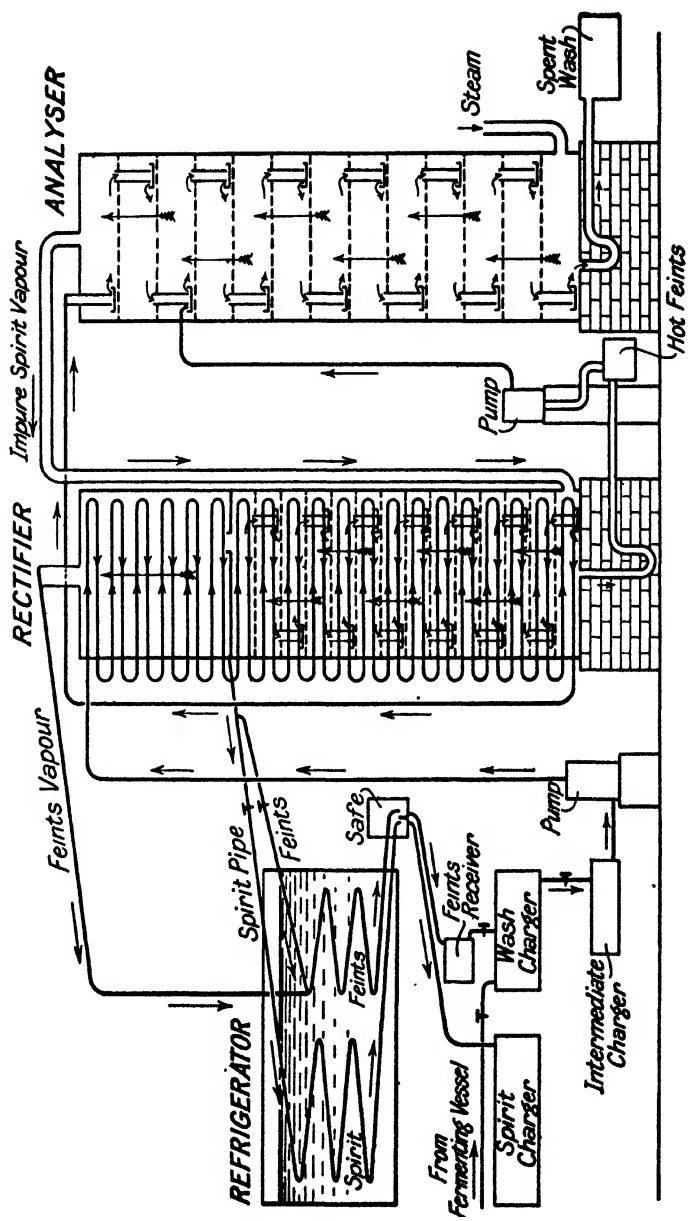
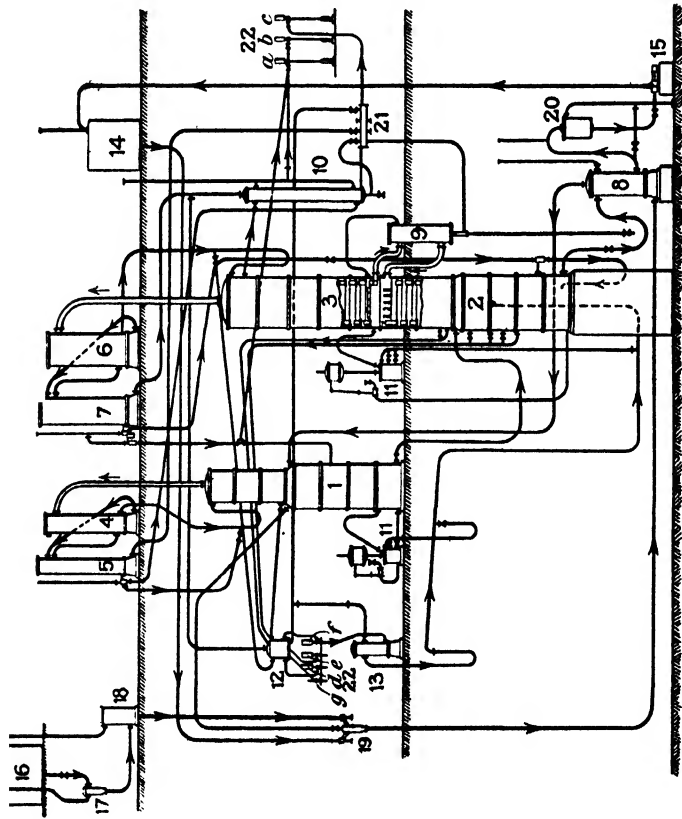
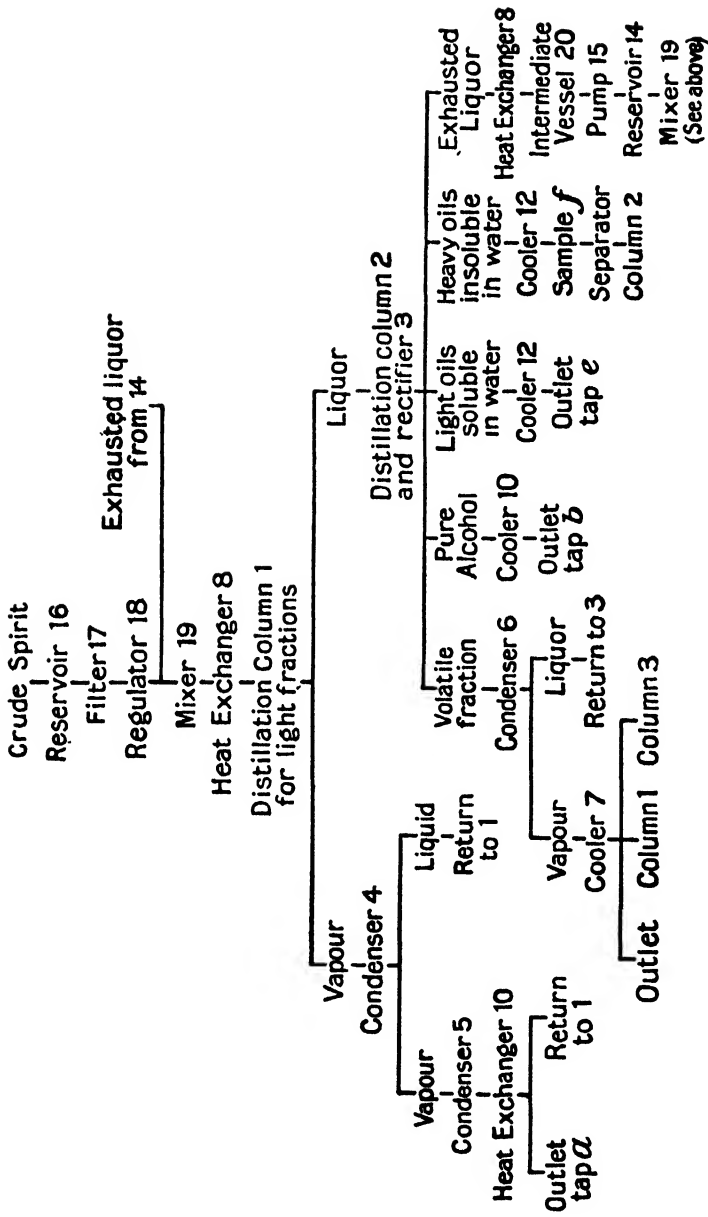


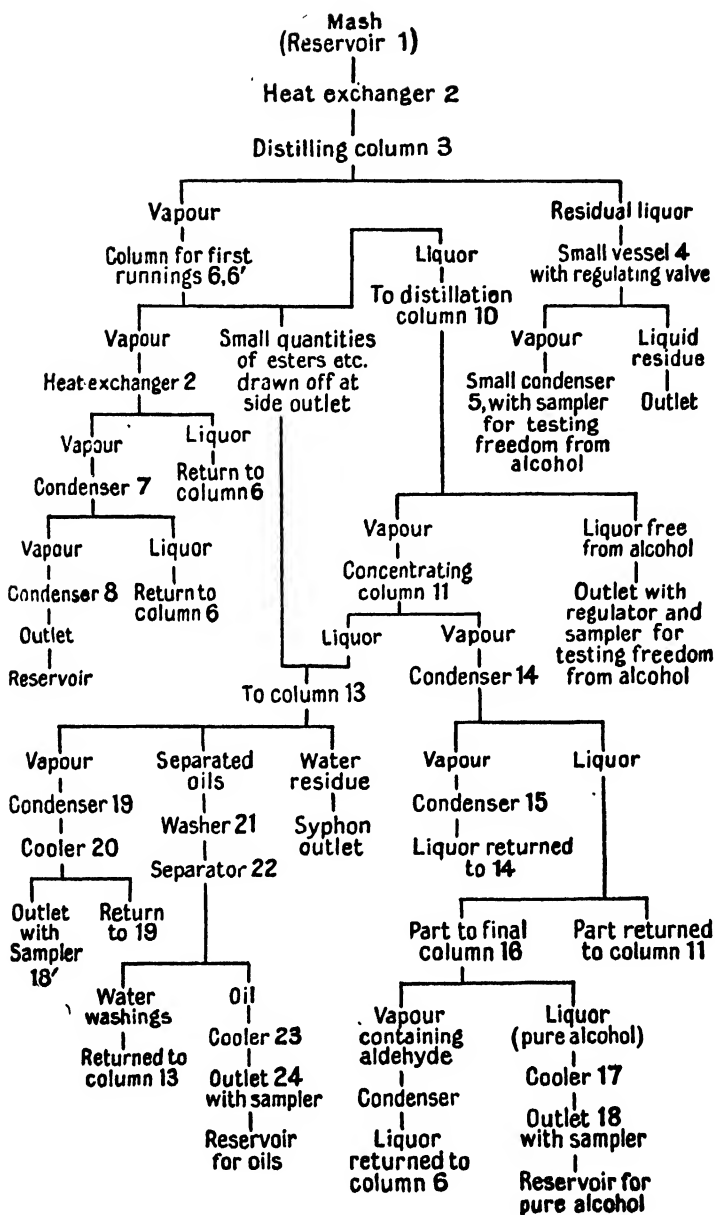
FIG. 4.—COFFEY'S PATENT STILL.



1. Column for first runnings.
2. Column for exhausting the liquors.
3. Rectifying column.
4. Condenser for first runnings.
5. Cooler for first runnings.
6. Condenser for rectifying column.
7. Cooler for rectifying column.
8. Preheater.
9. Cooler.
10. Cooler for rectified spirit.
11. Steam regulators.
12. Cooler for later distillates.
13. Decanter.
14. Reservoir for exhausted liquor.
15. Pump.
16. Reservoir for crude spirit.
17. Filter.
18. Regulator for rate of flow of crude spirit.
19. Mixer.
20. Intermediate vessel.
21. Water distributor.
22. Sampling vessels.

FIG. 5.—BARBET CONTINUOUS STILL FOR ALCOHOL; AND FLOW SHEET FOR SAME.





Patent Stills. These are much more effective stills, which are used for concentrating alcohol up to a strength suitable for industrial purposes (90 to 95 per cent. alcohol, by volume). The patent still otherwise known as the Coffey still, is largely used in this country, and is represented in Fig. 4. This is operated by steam on the counter-current principle. The wash enters at the top of the still and meets a current of steam entering at the bottom. The still-head contains a series of perforated diaphragms, and at each of these partitions a partial fractionation of the alcohol liquor takes place, so that by the time the wash reaches the bottom of the still it is depleted of its alcohol and passes out as a suspension of solid matter in plain water, whilst the alcohol vapour and steam, together with other volatile matter, pass upwards. In so doing, the vapour becomes continuously richer in alcohol as the steam condenses by giving up its heat to the descending liquor. The vapour which passes from the top of the still is led into a "rectifier" in which it is condensed fractionally. At first the water condenses, and the condensate becomes richer in alcohol as the vapour passes upwards through the cooled chambers. The liquor which ultimately condenses contains 90 to 95 per cent. by volume of alcohol. As this still is continuous in action, it forms a great improvement on the ordinary type of simple still in its capacity of output, and also gives a stronger spirit than can be obtained from discontinuous stills. Apart from the strong alcohol, weaker fractions are obtained in the rectifier, and these are returned to the still for further fractionation. When the distillation has continued for some time, the higher boiling alcohols (fusel oil) begin to accumulate in the liquor, and in order to recover these the temperature is raised after a time to distil off the fusel oil. This is condensed separately and the fusel oil which separates is skimmed off, and the remainder returned to the

still. Various other continuous stills are in operation on the Continent and in America (Figs. 5, 6).

In all cases the rectifying columns are fitted with bubblers to effect the fractionation of the vapour. Various types of these bubblers are shown in Fig. 7.

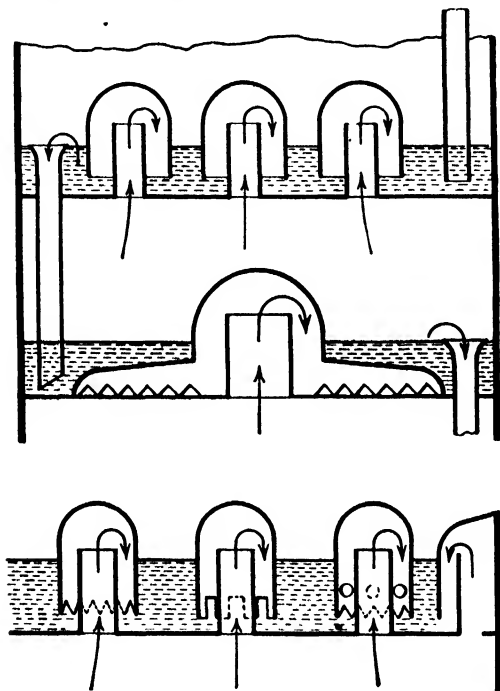


FIG. 7.—TYPICAL SECTIONS OF PARTITIONS IN DISTILLATION COLUMN, SHOWING DIFFERENT TYPES OF BUBBLERS FOR SPIRIT VAPOUR.

When an alcohol of extreme purity is required it is subjected to a further rectification in special stills (either continuous or intermittent). Frequently the alcohol is diluted with water before rectification, as this helps to remove impurities. Concentrated salt solution is also used. In some cases the purification is assisted by treatment with wood-charcoal.

As mentioned in Chapter II, it is impossible by fractionation to increase the alcoholic strength beyond about 96 per cent., since alcohol of this concentration forms a constant-boiling mixture with water. If absolute alcohol is required, dehydration by chemical means (for instance, by lime) must be employed.

CHAPTER V

VEGETABLE SOURCES OF ALCOHOL

UP to the present, the supplies of alcohol obtainable from such well-known sources as potatoes, grain, and molasses have sufficed for industrial requirements, in addition to the alcohol used for drinking purposes. The time is, however, rapidly arriving when supplies greatly in excess of those hitherto available will be urgently required. This is due mainly to the growing shortage of petrol for internal combustion engines.

Quantity of Alcohol Required. The quantities of alcohol used in this country for various manufacturing purposes are indicated in Table XI, p. 76. The following quantities of alcohol were made and used in the United Kingdom, United States, and Germany, taking the period 1909 to 1913 as a period of normal consumption (figures in millions of gallons of 100 per cent. alcohol).

	Millions of Imperial Gallons.		
	U.K.	U.S.A.	Germany.
Total alcohol made per yr.	26·0	72·2	82·9
Used as beverages . . .	18·2	56·4	46·7
Used in technical applications . . .	3·9	5·8	34·9

The quantity of alcohol which would be required to replace the petrol used for motors, or a proportion

of this, will be seen from the following table, showing the consumption of petrol.*

PETROL IMPORTED INTO UNITED KINGDOM.

(in millions of Imperial gallons)

1908.	1909.	1910.	1911.	1912.	1913.	1914.
42	52	55	68	80	101	120

The consumption of petrol in the United States is very much greater, as shown by the following table.†

CONSUMPTION OF PETROL IN U.S.A.

(in millions of Imperial gallons)

1914.	1915.	1916.	1917.	1918.
1,200	1,400	1,680	2,320	2,680

The consumption of petrol in the United Kingdom in 1920 was a little over 200 million gallons, and the requirements will undoubtedly increase.

Thus, if it became necessary to replace by alcohol 50 per cent. of the petrol now consumed in the United Kingdom, the yearly consumption of alcohol would be at least 100 million Imperial gallons of bulk spirit—a quantity which quite eclipses the requirements for manufacturing purposes. Obviously such a quantity of spirit can only be procured by enormous additions to our present sources of supply, and opinions are divided as to the possibility of meeting any substantial proportion of the demand for motor

* Tweedy, *Industrial Alcohol*, p. 5.

† From *Omd.* 218, p. 5.

spirit by the substitution of alcohol for petrol. Since, however, the supplies of petrol are becoming less and less adequate to meet the demand, the necessity for a substitute is very insistent, and the employment of vegetable instead of mineral sources is in itself attractive, as the vegetable products are renewable season by season with the help of solar energy, whereas the mineral sources, once used, cannot be replaced. In other words, by the use of mineral fuel we live on our capital, by the use of vegetable fuel we live on our yearly income.

The following statements as to possible supplies are of interest in this connection.

Heriot states* that if the whole of the world's supply of cane and beet molasses were used instead of being largely wasted, it would yield 200 million gallons of alcohol per year. A memorandum by the Fuel Research Board (July, 1920)† estimates, however, only 17 to 18 million gallons of 95 per cent. alcohol from this source within the Empire.

A report‡ is quoted to the effect that in the Pacific Islands, maize, cassava, and sugar cane could be grown and utilized so as to produce 50 million gallons of alcohol a year, and it is suggested that the world demands could be filled within certain Empire areas. An estimate of 6d. per gallon is given for the cost of the alcohol (excluding transport).

At a conference convened by the Imperial Motor Transport Council§ it was stated by Ormandy that a district in East Africa equal in area to the county of Kent could, with a suitable type of crop, give enough alcohol to take the place of petrol in the whole of the British Isles. At the same conference, Sir F. Nathan spoke less confidently of the prospects of substituting alcohol for petrol on account of the undesirability of drawing on food supplies and the expense of making alcohol from sawdust, etc. It was stated that alcohol has been manufactured for several years in Natal for power purposes with an output of 10,000 gallons a month, and that Australia was also making power-alcohol from raw materials imported from New Guinea. A new company in Australia|| expects to make 5½ million gallons, increasing to 18 million gallons per year.

* *J. Soc. Chem. Ind.*, 1915, Vol. 34, p. 336.

† *Chem. Trade J.*, 1920, Vol. 67, p. 108.

‡ *Times Trade Supplement*, 11th Sept., 1920.

§ *Chem. Trade J.*, 1920, Vol. 67, p. 531.

|| *Times Trade Supplement*, 12th June, 1920.

Competitive Price for Alcohol. Since the crux of the problem is the production of a supply of alcohol for motor purposes, the price of petrol must be taken as a guide to the price which would enable alcohol to enter into consideration for this purpose. The present retail price of petrol is 3s. 5½d. (1921) per gallon, whereas that of methylated spirit is about 10s. 6d. per gallon. This shows a disparity which would put alcohol out of court, if there were no prospect of cheapening it greatly. The yield of alcohol obtained on fermentation is so near to the theoretical that there is no material improvement to be looked for in this direction, but working costs might be reduced in other respects, for instance by continuous working. The removal of certain excise restrictions would assist greatly in this direction (Chapter III).

Breckler gave estimates of working costs, which indicated* that alcohol could with difficulty be produced to compete with petrol, even with a cheap raw material.

Capt. Desborough reviewed the possibilities of supplying† 95 per cent. alcohol at 3s. 2d. per gallon retail. He considered that 1s. would be absorbed in distribution and other charges, leaving 2s. 2d. for the manufacture and profit. The cost of manufacture would be about 9d. per gallon, including depreciation of plant, and 4d. per gallon might be allowed for interest on capital. This leaves 1s. 1d. to pay for the raw material. One ton of fermentable carbohydrates yields about 120 gallons of alcohol; hence the maximum admissible price for the pure carbohydrates is £6 10s. per ton. Taking the average percentage of carbohydrates in various materials, it is calculated that £6 10s. per ton for pure carbohydrates would correspond to £1 3s. for Jerusalem artichokes; the same for potatoes; 11s. for mangolds; 17s. for sugar mangolds (with 13 per cent. sugar); £6 8s. for maize; and £4 17s. for rice. Evidently a very cheap form of carbohydrates would be necessary to enable alcohol to be supplied at a cost which would compete with that of petrol. Maize, for instance, would have to come down from about £20 to £4 8s. per ton to compete on the above basis.

It is calculated‡ that alcohol can be retailed at 2s. per gallon from plants and trees in Papua.

* *Chem. and Met. Eng.*, 1917, Vol. 9, p. 612.

† *Brit. Assoc.*, 1920.

‡ *Times Trade Supplement*, 12th June, 1920.

Both on the ground of cost and on that of supply, it is evidently necessary to consider the vegetable materials which are prolific in growth and which yield a high percentage of alcohol on fermentation. It has frequently been assumed that it is only in tropical and sub-tropical countries that vegetable substances can grow sufficiently profusely to be worthy of study.* Capt. Desborough quotes figures, however, which show that root crops are more prolific in a temperate climate, and he urges the reclamation of land in this country for the production of crops from which alcohol may be obtained. Experiments in this direction are in progress at the R. N. Cordite Factory, Holton Heath.

Vegetable Sources of Alcohol. The vegetable materials from which alcohol may be obtained are (1) products containing sugar such as molasses, mowra flowers, sugar beet, and mangolds; (2) products containing starch or inulin, such as potatoes, artichokes, maize, etc; (3) cellulose in various forms, such as sawdust, peat, etc. Table VIII shows the principal raw materials which have come under consideration for this purpose.†

In reviewing the data from different sources, direct comparisons are frequently difficult, as some data are referred to proof spirit and others to 90 or 100 per cent. alcohol. The differences between the U.S.A. proof standard and the British standard, between Imperial and U.S.A. gallons, and between long and short tons also cause some confusion (see

* See, for instance, *Cmd.*, 218.

† This table has been compiled from data given by Tunison, *J. Frankl. Inst.*, 1920, Vol. 190, p. 372; Simmonds, *Alcohol*; Tweedy, *Industrial Alcohol*; Desborough, *Brit. Assoc.*, 1920; Sinkinson, *Beama Journal*, 1920, Vol. 7, p. 173; Ullmann, *Enzyklopädie der tech. Chem.*; and various scattered data from the *Chemical Trade Journal*, *Times Trade Supplement*, etc.

Appendix). The data in Table VIII have been reduced to the same units for comparison.

TABLE VIII.—COMPOSITION AND YIELD OF VARIOUS SOURCES OF FERMENTATION-ALCOHOL.

Sources arranged alphabetically.	Per cent. of Fermentable carbohydrates.	Yield of Alcohol (100%).		
		Per cent. by Weight.	Litres per 100 kg.	Imp. galls. per ton.
Acorns	40 to 50	12 to 16	15 to 20	34 to 45
Algae	—	10	12	28
„ marine	—	6	7	17
Arrowroot	30	—	—	—
Artichokes	16 to 18	7	9	20
Asphodel roots	—	5	6	14
Barley	53 to 60	25	31	70
Bassia or mowra flowers	60 to 67	24 to 35	30 to 45	67 to 100
Beet molasses	48 to 53	20 to 26	25 to 32	56 to 73
Buckwheat	—	24 to 29	30 to 36	67 to 81
Cassava or manioc	30	—	—	—
Corn cannery waste	—	7	9	20
Corozo or vegetable ivory	—	8 to 14	10 to 18	22 to 40
Horse-chestnuts	35 to 50	12 to 20	15 to 25	34 to 56
Maize	55 to 68	15 to 30	19 to 37	42 to 84
Mangolds	8.5	—	—	—
Nipa palm sap	14 to 16	6	7	17
Oats	53 to 56	22 to 26	28 to 33	62 to 73
Potatoes	18 to 20	7 to 9.5	9 to 12	20 to 27
„ sweet	27 to 29	11	14	32
Reeds (roots)	—	9	11	25
Reindeer moss	55	Over 20	Over 25	Over 56
Rice	67 to 83	23 to 36	29 to 45	65 to 100
Rye	55 to 63	24 to 29	30 to 36	67 to 81
Sawdust	(13)	6 to 16	8 to 20	17 to 45
Sisal waste	12	—	—	—
Sorghum or dari	60 to 65	29 to 32	36 to 40	81 to 90
Sotol	—	5 to 8	6 to 10	14 to 25
Sugar beets	8 to 18	4 to 8	5 to 10	11 to 22
„ cane	—	6 to 9	8 to 11	18 to 25
„ mangolds	13	—	—	—
„ molasses	52 to 67	25 to 29	31 to 36	70 to 81
Sulphite lye	1.5 to 2	0.7 to 1.0	0.9 to 1.2	2 to 3
Wheat	60 to 65	26 to 31	33 to 39	73 to 87

Numerous fruits contain sugars which can be converted to alcohol by fermentation, but these have not been included in the table, as they are in general too expensive to be considered as sources of industrial alcohol.

The following comments give some indications of

the investigations which have been made on various raw materials, and show which of these materials have been used on the manufacturing scale for fermentation purposes.

Algae (*laminaria digitata*). Experimental work is given by Kaysre*, also on marine algae (*laminaria flexicaulis* and *L. saccharina*).† The results are given in Table VIII.

Artichokes. These contain directly fermentable levulose. Under ordinary conditions they are too expensive as a source of alcohol, but the maximum crops obtainable might yield alcohol to compete with petrol.‡ Experiments are in progress at Holton Heath.

Asphodel (*asphodelus ramosus*) grows profusely on the shores of the Mediterranean and contains starch. Alcohol has been made from this plant in Algiers.

Bassia Flowers. The bassia tree, otherwise known as mowra, mahua, or Indian butter tree, grows in several species (1) in Ceylon, (2) in the forests of the central provinces of India, (3) in the Sub-Himalayan tract. The seeds contain an edible butter which was formerly exported to Germany and Belgium for margarine, soap, and candles. The flowers contain a high proportion of sugar, which could probably be increased by cultivation. The plant grows very profusely almost anywhere, and is regarded as a very cheap potential source of alcohol.§ The cost of the dried flowers at the factory is given as about 30s. per ton, and these would yield 24 to 35 per cent. by weight of alcohol. It is stated that there are already enough mowra trees for 750,000 gallons of proof spirit per year. Motor trials on the alcohol from this source have given good results.||

Beet Molasses. This forms the refuse from the beet sugar manufacture, and only needs dilution to be ready for fermentation. Heriot** calculates that the world's supply of beet molasses would yield 100 million gallons of 90 per cent. alcohol per year. Beet molasses are already largely used for alcohol production, especially in France.

* *Compt. rend. Acad. d. Agric.*, 1918, Vol. 4, p. 450.

† *Ann. Chim. Analyt.*, 1919, Vol. 1, p. 79.

‡ Desborough, Brit. Assoc., 1920.

§ *Times Trade Suppl.*, 31st July, 1920; *Chem. Trade J.*, 1920, p. 406; *Beama Journal*, 1920, Vol. 7, p. 175.

|| *J. Roy. Soc. of Arts*, Vol. 68, p. 444.

** *J. Soc. Chem. Ind.*, 1915, Vol. 34, p. 337.

Cactus. This has been used in Mexico for making spirit for drinking purposes, but its possibilities on a large scale have not been investigated.

Cassava or Manioc. This grows very luxuriously in tropical climates. It compares very favourably with potatoes in starch content, and contains in addition to 25 per cent. of starch some 4 to 6 per cent. of sugars. The tubers are 6 to 10 lb. in weight, and it is reckoned that an acre of land will produce more than twice as much starch when growing cassava as when growing potatoes.*

Corn Cannery Waste. This is used to some extent in the United States for the production of alcohol.† The waste amounts to 40 per cent. of the corn, not counting the husks as available.

Corozo or Vegetable Ivory. The seeds contain considerable quantities of mannocellulose which can be hydrolysed to mannose by boiling with dilute acids. The sugar can be fermented by suitable ferments, preferably assisted by sodium phosphate and ammonium sulphate. This can also be effected by moulds of the type *Mucor Rouxii*.‡

Maize. This contains mainly starch together with a small proportion (3 per cent.) of gum and sugar. It is a very important source of alcohol in America and France. At present prices it could not compete for power-alcohol, but Capt. Desborough§ is of the opinion that it could be produced in some parts of South America, such as Peru, at a very low figure—possibly £2 per ton. This would correspond to about £3 per ton for the available carbohydrates or a charge of 6d. per gallon of alcohol for raw material, which might yield alcohol at a retail price in the neighbourhood of 2s. 6d. It has been suggested that maize could be grown very cheaply in the Pacific Islands.

Mangolds. These contain 8.5 per cent. of fermentable carbohydrates, and sugar mangolds contain 13 per cent. At present prices they do not form a sufficiently cheap source for industrial alcohol.||

Nipa Palm (*Nypa fructicans*). This grows very thickly in the Philippine and Malay Islands, and it is stated that alcohol

* Press Bulletin No. 63, Bureau of Science, Manila, 1917.

† Tunison, *J. Franklin Inst.*, 1920, Vol. 190, p. 384.

‡ Mezzadrolì, *Boll. Chim. Farm.*, 1918, Vol. 57, p. 361.

§ Brit. Assoc., 1920.

|| Memo. of Fuel Research Board, July, 1920.

can be obtained from it at 20 cents per gallon (U.S.A.) corresponding to about 1s. per Imperial gallon at normal exchange.* The quantity available would yield 40 million Imperial gallons every season, but at present the production is only 2 million Imperial gallons per year. The untapped area amounts to 100,000 acres.

Peat. The possibility of utilizing peat for the production of alcohol has been much discussed. The Committee on Power-alcohol† reported that no satisfactory method of utilizing peat had come to its notice, but recommended that the potential value of this source should not be overlooked. Ullmann's *Enzyklopädie* gives an account of the processes which have been tried, but states that none of these has proved remunerative. According to Eckstrand, 5·2 per cent. of alcohol has been obtained from dried peat.

Polymnia Edulis. This is a tuberous plant which grows in the Andes at a height of 6,000 ft., and has been the subject of experiment in France and at Holton Heath.‡ The sugar content is stated to compare favourably with that of mangolds.

Potatoes. These are widely used in Europe, and to an increasing extent in America. Although containing only about 20 per cent. of starch, as compared with 70 to 80 per cent. in corn, etc., they give a much higher yield of alcohol per acre. In Germany, about 80 per cent. of the alcohol is made from potatoes, amounting to 70 million gallons in 1912 or 1913, whilst in France beet, maize, and molasses are mainly used. A ton of potatoes yields about 20 Imp. galls. of alcohol, or in the case of sweet potatoes 35 galls.

At present prices potatoes cannot yield alcohol at a price to compete with petrol,§ but it appears possible that the yield of potatoes per acre might be increased materially.|| Potatoes require a good soil and heavy manuring, but leave the soil in very good condition for later crops. The present yield per acre is higher in the United Kingdom than in other countries, but the area of land under potatoes is relatively small. It appears probable that a very large additional supply of alcohol could be made available for industrial purposes if the growing of potatoes in this country were encouraged, and if co-operative schemes were set on foot as in Germany.

* *Commerce Reports*, 12th July, 1920, p. 212.

† *Cmd.*, 218, p. 6.

‡ Desborough, *Brit. Assoc.*, 1920.

§ Cf. Desborough, *Brit. Assoc.*, 1920, and Memo by Fuel Research Board, July, 1920.

|| Tweedy, *Industrial Alcohol*, pp. 18, 19.

Prickly Pear. This grows very profusely in Australia, and is known to be capable of fermentation,* but no definite data appear to be available to show the yield of alcohol which is obtainable. .

Reeds. The roots of the common reed (*arundo phragmites*) can be used for making alcohol.†

Reindeer Moss (*Cladornia rangiferina*) contains hemi-celluloses which can be converted to alcohol.‡ The work so far is apparently only experimental.

Rice contains a large proportion of starch, and gives a high yield of alcohol, but is too costly to form a cheap source of alcohol. Rice-straw is being tried experimentally in India.§

Sawdust. On account of its cheapness, this has attracted a good deal of attention as a possible source of alcohol. It consists essentially of cellulose, part of which can be hydrolysed to fermentable sugars. It is of interest to mention that this hydrolysis of wood has been known for more than 100 years (Braconot, 1819). Simonsen succeeded in 1898, in converting 45 per cent. of the cellulose to sugars by heating with dilute acid under pressure. Classen showed that wood cellulose could be converted to sugar by sulphurous acid at 120 to 140°C. A factory has been operated on this principle at Chicago. The plant consisted of an apparatus for the production of sulphurous acid, a converter in which the acid acted on the wood, a battery of dissolvers, neutralization vessels, fermentation vats, and stills. This process has, however, been superseded by a direct hydrolysis with dilute sulphuric acid.|| It is impossible to convert the cellulose completely to sugar, as the sugar decomposes if the heating is prolonged.** Furfurol is formed as a by-product in the hydrolysis, and this compound is present to some extent in the finished spirit.

Two plants are at work in America.†† Breckler states that the process is not cheap enough for motor spirit. Kressmann

* *Chem. Trade Journ.*, 1920, Vol. 67, p. 531.

† D.R.P. 311217 of 1916.

‡ Ellrodt and Kunz, *Brennerei Zeit.*, 1918.

§ *Times Trade Suppl.*, 25th Sept., 1920.

|| For details see Kressmann, *Met. and Chem. Eng.*, 1916, Vol. 15, p. 78.

** Ost and Wilkening, *Chem. Ztg.*, 1910, p. 461.

†† Kressmann, *Met. and Chem. Eng.*, 1916, Vol. 15, p. 78; Alcohol Conference, *Met. and Chem. Eng.*, 1916, Vol. 15, p. 480; Breckler, *J. Ind. Eng. Chem.*, 1917, Vol. 9, p. 612; Tunison, *J. Frankl. Inst.*, 1920, Vol. 190, p. 384; Ullmann, *Enzyklopädie*.

quoted costs of 13.7 to 19.5 cents per gallon (1916.) Nathan considered that the present cost was too high for power purposes.*

According to a pamphlet from the U.S.A. Forest Products Laboratory† alcohol can be produced from wood waste at about 25 cents per U.S.A. gallon. Soft woods are best; thus white spruce yields 25.8 galls. per ton and longleaf pine 25.1 gallons, whilst hard maple yields only 9.1 gallons.

Laskowsky‡ claimed yields of about 25 Imp. galls.

In Switzerland hydrochloric acid is being used, apparently with success.

The possibility of converting cellulose to alcohol by means of moulds is being investigated.§ If these experiments are successful, a new and highly promising field will be opened up.

Sisal Waste. This has been converted to alcohol in Yucatan. The leaves contained 12 per cent. of sugar, rising to 14 per cent. after a long, dry season. Experiments have also been made in British East Africa with some success.||

Sorghum. This contains levulose and crystallizable sugar. It grows very readily and flourishes over an extensive part of the earth's surface. It gives a high yield of alcohol, and may become an important source of supply. A new Company in Australia intends to manufacture alcohol on an extensive scale from sorghum on a co-operative system.**

Sotol. This plant grows in large quantities in N. Mexico and W. Texas, and is used for making alcohol.††

Straw. Experiments have been made by Ford,‡‡ which are stated to have been successful, but details of yield and cost are not available.

Sugar Beets. These are extensively used in France for the production of alcohol, but do not under present circumstances provide an alcohol sufficiently cheap to serve as a motor spirit in place of petrol.

* Conference Imp. Motor Transport Council, *Chem. Trade J.*, 1920, Vol. 67, p. 531.

† *J. Soc. Chem. Ind.*, 1921, Vol. 40, 69 R.

‡ *Chem. Ztg.*, 1919, Vol. 43, 51.

§ Desborough, Brit. Assoc., 1920.

|| Further information as to methods is given in *Tropical Life*, 1917, Vol. 13, p. 155, and *Bull. Agric. Intell.*, 1918, Vol. 9, p. 988.

** *Times Trade Suppl.*, 12th June, 1920.

†† U.S. Com. Rep., 2nd May, 1918.

‡‡ *Oil and Gas Journal*, Vol. 18, p. 36.

Sugar Cane is also too expensive for the production of power alcohol.

Sugar Corn Stalks. These contain a certain proportion of sucrose which may be utilized for the production of alcohol.

Sugar Molasses. This forms the chief source of alcohol in the United States.* Its utilization is of somewhat recent origin, but has attained enormous dimensions, the molasses being transported in large quantities in tank-cars and tank-steamers.† Large quantities of molasses are, however, still wasted. Thus in Queensland hundreds of thousands of gallons yearly are run into the rivers.

It is calculated that the alcohol (90 per cent.) obtainable from the world's supply of sugar cane molasses would amount to 100 million gallons if the whole were utilized.‡ The output from Cuba molasses has been estimated at 40 million gallons (probably U.S.A. measure) from $2\frac{1}{2}$ million tons of molasses.§ A much lower estimate is, however, given by the Fuel Research Board.||

Details of cost were given by Heriot (loc. cit.) from which he estimated that the denatured alcohol could be sold for 15 cents per gallon (1915). He quoted other authorities who gave the following costs per gallon (excluding the cost of the molasses, i.e. conversion costs only) U.S.A., 8 cents; Demerara, 5 cents, excluding fuel; Hawaii, 10.2 cents; Cuba, 10 cents; average about 5d. per gallon (1915). The yields under different conditions are given by Magne.**

Sulphite Liquors. These form a by-product of the paper pulp mills, and a large amount of work has been done with the object of converting the carbohydrates which they contain to alcohol. In one process, the liquor is treated with a soluble barium compound under oxidizing conditions whereby the sulphur compounds are precipitated. After separation of the sludge, the liquor is fermented. In another process, the liquor is treated with barium sulphide under oxidizing conditions and the barium sulphide is regenerated by treating it under pressure with the carbon dioxide evolved from the fermentation vats. In a further process†† the liquors are cooled, partially freed from sulphur dioxide, and fermented in a current of air.

* For statistics, see West, *J. Soc. Chem. Ind.*, 1920, Vol. 39, 380R.

† Tunison, *J. Frankl. Inst.*, 1920, Vol. 190, p. 386.

‡ Heriot, *J. Soc. Chem. Ind.*, 1915, Vol. 34, p. 336.

§ Tweedy, *Industrial Alcohol*, p. 28.

|| Memo, July, 1920.

** *Louisiana Planter*, 1917, Vol. 59, 13.

†† McKee, Brit. Pat. 120520, U.S. Pat. 1273392.

Sulphite liquor is deficient in nitrogenous nutrients, phosphoric acid, potash, and magnesia. It has been proposed to supply these ingredients by the use of hydrolysed seaweed in conjunction with the sulphite liquor, and this has apparently given promising results on an experimental scale.* Three plants are at work on the conversion of sulphite liquor to alcohol in the United States.† Opinions vary as to the degree of success of the process. Breckler states that the alcohol is too costly for motor spirit. On the other hand, the Honorary Advisory Council for Scientific and Industrial Research of Canada reports that the sulphite liquor from all the pulp mills in Canada could supply 5 million gallons of 95 per cent. alcohol per annum at about 1s. 6d. per gallon. It has been pointed out by Desborough‡ and also by Tunison§ that many of the factories are not large enough to have their own fermentation plants and the cost of transport would be prohibitive; moreover, the cost of acid would be considerable. Sinkinson|| states that the yearly production of sulphite lye in Norway corresponds to 17 million litres of alcohol, which would render Norway self-supporting. In Sweden, there are four established spirit factories working from sulphite lye, producing 3 million litres per annum, and 14 more factories are in course of erection. The total output in Sweden may reach 36 million litres.

Sulphite liquor must thus be looked upon as an auxiliary source of cheap alcohol, but is not capable of indefinite expansion as it is limited to the amount of sulphite liquor available.

White Moss grows profusely in Sweden, and the County Syndicate Aktiebolag has petitioned the Swedish Government for permission to make 5,000,000 litres of spirit from this moss under official supervision.**

From the above review it is seen that a very wide range of vegetable substances might be brought into use for the production of alcohol. Some of the raw materials appear to offer possibilities of cheap supplies of alcohol, as, for instance, bassia flowers, sorghum, cassava, nipa palm sap, sulphite lye, sawdust, and possibly maize, artichokes, and others.

* *Pap. tech. Forening*, 9th April, 1919; *Papierfab*, 1919, Vol. 17, p. 1052.

† Breckler, *J. Ind. Eng. Chem.*, 1917, Vol. 9, p. 612.

‡ Brit. Assoc., 1920.

§ *J. Frankl. Inst.*, 1920, Vol. 190, p. 384.

|| *Beama Journal*, 1920, Vol. 7, p. 176.

** U.S. Commerce Reports, 1918.

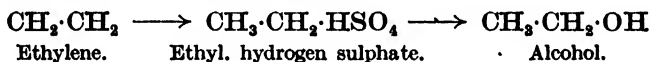
In Germany, a co-operative system has long been in operation, in which a cluster of farms supplies the crops (mainly potatoes) required for a central distillery, and the residual products are returned to the farms as feeding-stuffs. The adoption of a similar system in this country has been strongly urged by some writers.*

* Cf. Tweedy, *Industrial Alcohol*, 1917.

CHAPTER VI

SYNTHETIC ALCOHOL

Alcohol from Ethylene. The formula of alcohol C_2H_6O , differs from that of ethylene, C_2H_4 , by one molecule of water, and the ordinary laboratory method of making ethylene is from alcohol and sulphuric acid. It seems, therefore, a somewhat curious inversion that it should be proposed to manufacture alcohol from ethylene. It is of interest to note that the first synthesis of alcohol, by Hennell in 1828, was from ethylene. The union of this compound with water can be readily effected by passing the ethylene through strong sulphuric acid with which it unites to form ethyl hydrogen sulphate. This is decomposed when boiled with water, forming alcohol and sulphuric acid.



Fritzsche foresaw the possibility of converting the ethylene in coal gas and coke-oven gas into alcohol,* and investigated the conditions necessary for the absorption in sulphuric acid and recovery of the alcohol, but the process did not succeed in practice on account of the large scrubbing plant which was necessary. He stated that 100 kg. of sulphuric acid absorbed 14 kg. of ethylene, from which 18 kg. of alcohol could be obtained.

Experiments at Skinningrove. In 1912, Mr. Bury, of the Skinningrove Iron Works, initiated an exhaustive investigation on the recovery of ethylene from the coke-oven gas of the Durham district, for the

* *Ch. Ind.*, 1897, Vol. 20, p. 266 ; 1912, Vol. 35, p. 637.

production of alcohol and its derivatives. The normal quantity of ethylene in coke-oven gas from Durham coking coal being about 2 per cent. by volume, it was reckoned that if 70 per cent. of the ethylene present could be extracted in the form of ethyl hydrogen sulphate, and this could be converted to alcohol with an efficiency of 70 per cent., a yield of 1.6 gallons of absolute alcohol would be obtained per ton of coal. Thus a carbonizing plant of the size of Skinningrove, dealing with 5,800 tons of coal per week, would produce 9,200 gallons of absolute alcohol per week.

The total quantity of coal coked in by-product coke-ovens in this country in 1918 was 14,635,403 tons. A yield of 1.6 gallons of alcohol per ton would correspond to 23,416,640 gallons of alcohol per year. If the country's gasworks were to recover their possible ethylene an additional quantity of 27 million gallons would be available.

The development of this project is given in a paper by Messrs. Bury and Ollander, before the Cleveland Institution of Engineers on 15th Dec., 1919, from which most of the following information is taken. The author is indebted to the Skinningrove Iron Works for permission to include this information.

The course of the experimental work at the Skinningrove works was somewhat diverted from its original course by the war demand for ethylene, as such, for the purpose of making dichloro-diethyl-sulphide (mustard gas), and a joint research of the Ministry of Munitions and the Skinningrove Company was undertaken, experiments being carried out at the works and at the Universities.

Absorption of Ethylene by Charcoal. The method used in these experiments depended upon the absorption power of charcoal. After abstraction of hydrogen sulphide, carbon disulphide, carbon dioxide and moisture by ordinary means, the heavy hydrocarbons

(benzene, etc.) and the ethylene hydrocarbons could be absorbed by beech charcoal, which after saturation would be removed from the gas and heated to yield ethylene and its homologues. It was found later that peat charcoal was an equally good absorbent, and was advantageous in other ways. The actual manufacture of ethylene in this way on the large scale did not mature, as the armistice intervened.

Absorption of Ethylene by Sulphuric Acid. For peace purposes, the isolation of ethylene gas serves no useful purpose, and it is considered preferable to absorb the ethylene directly from the gas by sulphuric acid on the grounds that (1) the handling of the solid charcoal is somewhat difficult, (2) it is necessary to free the gas from carbon dioxide, otherwise this gas is absorbed to the exclusion of the ethylene, (3) the fuel expenditure is greater in the case of the charcoal, (4) the maximum absorption of ethylene by charcoal is 1 per cent. of the weight of the latter, and thus a large quantity of charcoal has to be handled. Sulphuric acid on the other hand can absorb 5 per cent. of its weight of ethylene. Further, sulphuric acid is a coke-oven product, so that its use renders the plant more nearly self-contained.

On the other hand, a portion of the sulphuric acid is reduced to sulphur dioxide, which must be recovered and utilized. It is also necessary to guard against the conversion of the ethylene to ethyl ether by the sulphuric acid. Whichever absorbent is used, it is necessary to pay great attention to the economy of fuel in the recovery process, bearing in mind that the sulphuric acid has to be re-concentrated after use.

It is found that 70 to 80 per cent. of the total ethylene present in the gas can be absorbed by sulphuric acid of 95 per cent. concentration, at temperatures between 60° and 80°C. On hydrolysis of the ethyl hydrogen sulphate, 70 per cent. of the

possible quantity of alcohol is recovered. The deficit in yield is probably due to the presence of higher homologues of ethylene.

The absorption of ethylene by sulphuric acid has also been studied by Plant and Sidgwick.*

Effect on Heating Value of the Gas. Naturally, the abstraction of ethylene from gas lowers the heating value of the latter. Figures given by Bury and Ollander (*loc. cit.*) show that the ethylene hydrocarbons provide 6.86 per cent. of the heating power of coke-oven gas. If 70 per cent. of the ethylene hydrocarbons present be abstracted, this represents 4.7 per cent. of the heating power of the gas. In point of fact, the drying of the gas, which is a necessary part of the process, leaves the remainder of the gas richer than before in combustible gases, and this approximately balances the abstraction of the ethylene, as shown by the figures in Table IX.

TABLE IX.—CALORIFIC VALUE OF COKE-OVEN GAS BEFORE AND AFTER ABSTRACTION OF ETHYLENE.

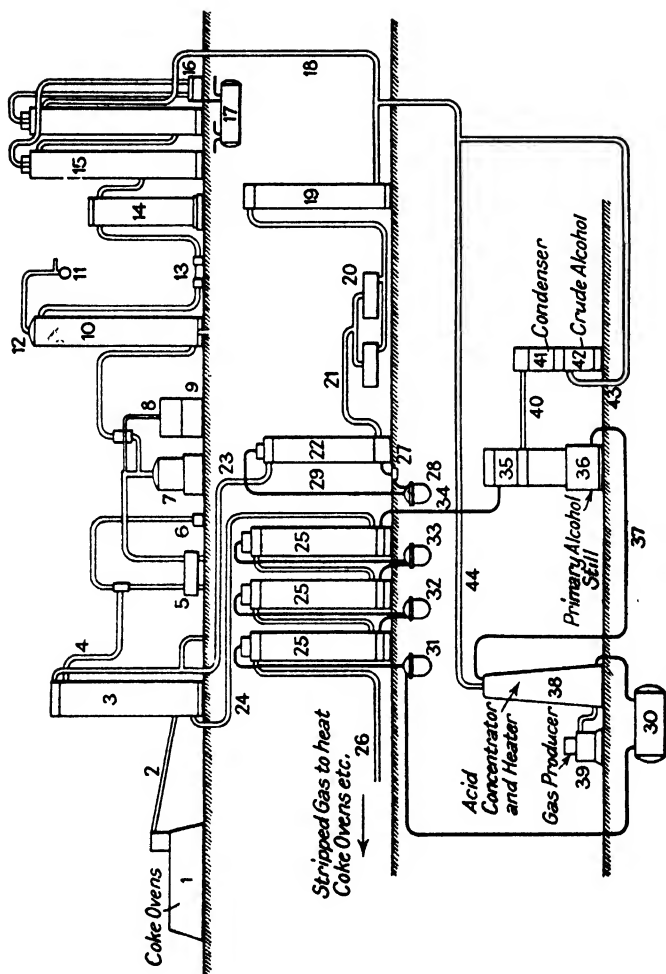
Constituent.	Inlet Gas.		Outlet Gas.	
	Volume per cent.	Calorific Value B.Th.U. per cu. ft.	Volume per cent.	Calorific Value B.Th.U. per cu. ft.
C_2H_4	2.0	32.1	0.62	9.95
CO	5.4	17.6	5.61	18.29
CH_4	25.0	255.0	25.96	264.79
H_2	50.0	163.0	51.91	169.23
CO_2	2.0	—	2.08	—
O_2	0.5	—	0.52	—
N_2	{ 15.1 }	—	13.30	—
H_2O		—	0.00	—
Total		467.7		462.26

* *J. Soc. Chem. Ind.*, 1921, Vol. 40, 14T.

A loss in volume of the gas is, however, naturally incurred when the moisture and ethylene are abstracted, and the process is advantageous only by reason of the much higher value of alcohol as compared with the total loss of heat units in the gas. The stripped gas is returned to the gas main, and used for its ordinary purposes. Ethylene is one of the main illuminating constituents, and from this point of view the gas suffers considerably. For most purposes, however, this is of minor importance.

Method of Working Plant for Alcohol from Coke-oven Gas. The diagram in Fig. 8 shows the sequence of operations. The hot gases from the ovens 1 pass from the hydraulic main 2 to a heat exchanger 3, and thence to the usual plant for the recovery of tar, ammonium sulphate, naphthalene, and benzol. No. 5 is a tar spray, 6 the tar pump, 7 the saturator, and 8 the centrifugal drier of the ammonium sulphate plant; 9 is the sulphate store; 10 is the naphthalene scrubber; 11 its water pump; 12 the water spray; and 13 the exhauster; 14 is a cooler; 15 the benzol scrubbers; and 16 wash oil pumps; 17 is a storage tank for wash oil. The cooled gas, after removal of these products, passes through pipe 18 to a hydrogen sulphide purifier 19, and then through ferric oxide in purifiers 20, and thence through pipe 21 to a moisture absorber or scrubber 22, in which 80 per cent. sulphuric acid is circulated. The gases then pass through pipe 23 to the heat interchanger 3, in which they are heated by the gases from the carbonizing plant, and thence through pipe 24 to the ethylene scrubbers 25; the de-ethylenated gas issuing from these scrubbers at 26 passes out to mains conveying it away for use in the heating of coke ovens, to the steel-works, gas engines, and soaking pits.

No. 27 is an acid catch-tank and 28 a blowing egg or elevator, by which the sulphuric acid is pumped through pipe 29 to the top of the scrubber 22.



Sulphuric acid (95 per cent.) is supplied from the tank 30 and blowing egg or elevator 31, to the last of the olefine scrubbers 25, passing in counter-current to the flow of the gas. From the bottom of the last scrubber 25, the acid is received in another elevator 32, which supplies it to the top of the second scrubber, from the bottom of which a third elevator 33 supplies it to the first scrubber 25. The temperature in the scrubbers 25 is maintained at 60 to 80°C, which is the optimum for absorption. The acid after absorption, issuing from the first scrubber 25 at which the gas enters, passes through pipe 34 and a heat exchanger 35, to a primary alcohol still 36; thence the acid flows through pipe 37 to an acid concentrating and heating plant 38 (Gaillard tower) to which heat is supplied from a producer 39 fired with cooke-breeze or other practically waste fuel. The re-concentrated acid from the plant 38 passes out to the tank 30, whence it is circulated again through the scrubbers 25, fresh acid being supplied as required to make up for that which is consumed in the process.

Pipe 40, from the alcohol-still, leads to a condenser 41, in which the crude alcohol is collected at 42. A pipe 43 from the condenser, and a pipe 44 from the acid concentrating and heating plant 38, convey sulphur dioxide gas, which is evolved as a reduction product, to the hydrogen sulphide purifier 19, where it reacts with the hydrogen sulphide in the coal gas, producing sulphur. This sulphur is removed and conveyed to a sulphur-burning plant, wherein it yields sulphuric acid for use in the scrubbers 25 and in the plant 7 for making ammonium sulphate.

Prospects of Ethylene Process. As to the commercial prospects of this method of preparing alcohol, it is impossible to speak with certainty. It entails the use of large volumes of sulphuric acid, and would require an extensive concentrating plant. The experiments have not proceeded far enough on the

commercial scale to give definite indications of the cost. Grady* gives a figure of 15·3 pence per gallon of 90 per cent. alcohol. Capt. Desborough† mentions an estimate of 2s. per gallon. The Committee on Power Alcohol‡ speaks of ethylene as a large potential source of power alcohol, but considers that further investigations are necessary, particularly as regards the conversion of the ethylene into alcohol, before definite figures as to quantity and price can be given.

An article by de Loisy§ should be referred to in this connection. It had been found previously that the absorption of ethylene by concentrated sulphuric acid could be greatly accelerated by catalysts such as vanadium, uranium, tungsten, etc. De Loisy proposed to apply this to coke-oven gases, but had so far made only small experiments on the gas supply of Paris. He reckoned that the pre-war consumption of coal in coke-ovens in France would yield 760,000 hectolitres of alcohol per year.

Further experimental work on the Skinningrove process has been described by Tidman, who also quotes some results of trials in motors.||

Alcohol from Calcium Carbide. The industrial application of the electric furnace to the production of calcium carbide has led to an extensive development of products which can be derived from this compound. These include cyanamide, which is of importance as a fertilizer; and acetylene, which has important uses for illuminating purposes and for welding, apart from which it yields derivatives which are of commercial importance (acetic acid, various chlorinated products, etc.).

* *U.S.A. Commerce Reports*, 1919, No. 219, p. 1460.

† *Brit. Assoc.*, 1920.

‡ *Cmd.*, 218.

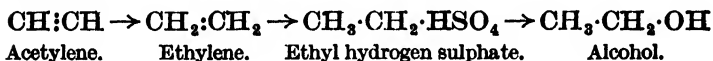
§ *Comptes rendus*, 1920, Vol. 170, p. 50; cf. *Brit. Pat.* 152495, *J. Soc. Chem. Ind.*, 1920, Vol. 39, 833A.

|| Joint Meeting of Soc. Chem. Ind. Newcastle and Cleveland Inst. of Engineers, cf. *J. Soc. Chem. Ind.*, 1921, Vol. 40, 86 T.

The production of alcohol from acetylene will be dealt with only briefly, as calcium carbide is primarily a product of countries in which cheap water power is available, a condition which does not apply to Great Britain, though the Dominions are more favourably situated in this respect.

Alcohol may be obtained from acetylene in two ways—

(1) By conversion to ethylene and thence to alcohol—



The conversion of acetylene to ethylene may be effected in various ways, as, for instance, by the action of hydrogen in presence of palladium-nickel.* The ethylene is absorbed in sulphuric acid, as described earlier in the present chapter.

(2) By conversion to acetaldehyde and thence by reduction to alcohol—



Acetylene is converted to acetaldehyde by passing the gas into dilute acid in presence of a mercury salt as catalyst.† Care must be taken to avoid loss of aldehyde by evaporation, as it boils at 22°C. The aldehyde is converted to alcohol by catalytic reduction, a mixture of aldehyde and hydrogen being passed over finely divided nickel at 140°.‡ Electrolytic reduction may also be used.§

The first step of the process (conversion of acetylene to aldehyde) has been extensively developed in

* D.R.P., 149,893, 253,160, 287,565, 295,976.

† Hibbert and Morton, U.S.Pat. 1213486, 1213487/1917; Dreyfus, Fr.Pat., 479656/1914; Consortium f. Elektr., Brit. Pat. 5132/1915.

‡ Sabatier and Senderens, *Comptes rendus*, 1903, Vol. 137, p. 301.

§ Chem. Fabrik Griesheim Elektron, Ger. Pat. 328342.

connection with the acetic acid industry, and large factories are in existence for the utilization of the process.*

Practical Application of Acetylene Processes. As to the conversion of aldehyde to alcohol on the large scale, the information is somewhat indefinite.

In 1895, Krüger and Pückert† stated that the process could not be worked so as to be remunerative, but considerable improvement in methods has since been made. In 1918, Beyer‡ stated that the process was likely to compete successfully with fermentation in Switzerland, owing to the low cost of power. Kent§ stated that installations were started in Switzerland which would produce 7,500 to 10,000 tons of alcohol per annum, by the aldehyde and ethylene methods. Capt. Desborough|| quotes a report of the German Government (1918) according to which a Swiss firm contracted to supply alcohol to the Swiss Federal Government at about 1s. per gallon. It is further stated, however, that the factory in question closed down, finding the manufacture of alcohol unprofitable. According to Simmonds** a process of making alcohol from acetylene was probably in use in Germany in 1918. The production of alcohol from carbide in Germany was to be reserved to the State (Imperial Spirit Monopoly Bill, 1918).

On the whole, it must be said that synthetic methods for the preparation of alcohol, although offering some promise, are insufficiently developed to be relied upon in the near future for supplies of industrial alcohol.

* Rooney, *Chem. and Met. Eng.*, 1920, Vol. 22, p. 847.

† *Ch. Ind.*, Vol. 18, p. 454.

‡ *Schweiz. Chem. Zeit.*, Vol. 2, p. 12.

§ *U.S.A. Commerce Reports*, 1917, No. 102, p. 426.

|| *Brit. Assoc.*, 1920.

** *Alcohol*. v. 101.

CHAPTER VII

TECHNICAL APPLICATIONS OF ALCOHOL

Annual Consumption for Technical Purposes. The uses of alcohol are by no means confined to drinking purposes, though it must be admitted that the major portion of the alcohol which is manufactured is thus used. Table X shows the proportion of alcohol used for technical purposes and as beverages in various countries in the period 1909-13, this being taken as the last period when conditions were normal; data for the war-period would be affected by abnormal conditions (explosives manufacture, etc.), and might thus be misleading.

TABLE X.—ANNUAL PRODUCTION AND UTILIZATION OF ALCOHOL (1909-13).

	Millions of Imperial gallons of 100% Alcohol.		
	Total Produc- tion.	Used in Bever- ages, etc.	Used for Technical purposes.
United Kingdom	26·0	18·2	3·9
France	59·3	42·3	14·7
Germany	82·9	46·7	34·9
Italy	9·4	6·1	2·3
Russia	125·9	97·3	8·8
Austria-Hungary	60·6	42·7	10·4
United States	72·2	56·4	5·8*

* 3 years' average.

It is at once striking that the United Kingdom took a low place in production, and that the alcohol

used for technical purposes was very much higher in Germany and France than in this country.

TABLE XI.—CONSUMPTION OF INDUSTRIAL ALCOHOL IN THE UNITED KINGDOM (1913).

Industrial Uses.	Imperial gallons.	Industrial Uses.	Imperial gallons.
<i>In the manufacture of :</i>		<i>In the Manufacture of</i>	
Finish, for sale	395,739	(<i>cont.</i>) :	
Varnishes for polishes or lacquers for sale	983,694	Photographic plates and papers, and other photographic purposes	46,144
Stains, paints, enamels, etc., for sale	67,546	Steel pens	3,498
Varnishes, finish, stains, polishes, lacquers, etc., or for polishing purposes in manufacturers' own workshops	300,325	Silk, crape and embroidery	8,450
Felt and other hats	134,742	Artificial flowers, etc.	5,060
Celluloid, xylonite, and similar substances	28,818	Rubber	586
Oilcloths, leather cloths, pegamoid and similar substances	215,937	Artificial silk	750
Linoleum and similar substances	5,340	Ships' compasses, spirit levels, etc.	1,081
Smokeless powders, fulminates and other explosives	19,260	Inks	799
Soap	180,708	Collodion	8,191
Electric lamp filaments	9,151	Disinfectants	2,311
Electric cables	5,070	Hop extract	10,000
Incandescent mantles	16,175		
Ether	198,113	<i>Other uses :</i>	
Chloroform	5,753	Dyeing and cleaning operations in laundries and dye works	42,170
Ethyl chloride and bromide	806	Textile printing	8,437
Solid medicinal extracts	53,663	Preservation of specimens in museums and hospitals	6,608
Alkaloids and fine chemicals	32,486	Educational and scientific purposes in colleges and schools	5,821
Embrocations, liniments and lotions	34,106	Analytical and scientific purposes in the laboratories of analysts' works, chemists, etc.	5,691
Surgical dressings	10,032	For hospitals, asylums, and infirmaries	51,218
Capsules and other medicinal appliances	2,016	Electrotyping and printing	1,132
Hair washes	29,497	Miscellaneous uses	10,905
Cattle medicines	2,547	For Admiralty dockyards and War Office arsenals and workshops, chiefly for varnishes and polishes	14,860
Plant washes, insecticides and sheep dips	10,877		
Aniline and other dyes : Solids	211	Total	2,990,870
Solutions	2,345		
Fireworks and matches	3,107		

The manifold technical applications of alcohol may be seen from Tables XI and XII, and the quantities will give some idea of the relative importance of the various demands for alcohol.

TABLE XII.—CONSUMPTION OF INCOMPLETELY DENATURED ALCOHOL IN GERMANY (1912).

Industrial Uses.	Imperial gallons.	Industrial Uses.	Imperial gallons.
Manufacture of vinegar	3,295,000	Chloroform . . .	5,000
Manufacture of vinegar for industrial purposes and for manufacture of acetates .	72,000	Iodoform . . .	5,000
Brewer's glaze . . .	29,000	Ethyl bromide and bromoform . . .	1,500
Finishing of rubber goods	2,000	Iodine or bromine containing fats for medicinal uses . . .	1,900
Celluloid and pegamoid	922,000	Lac dyes	92,000
Synthetic camphor . .	8,000	Brewers' pitch . . .	90
Sulphuric ether . . .	716,000	Feeding of gas lamps .	1,200
Sensitive films, paper, and plates for photographic purposes . .	46,000	Finishing of silk ribbons	1,700
Electrode plates for electric accumulators	20	Cleaning of jewellery and fine metal ware .	900
Acetic ether	13,000	Lacquers of all kinds (exclusive of brewers' glaze and lac dyes) .	700,000
Adhesive preparations	460	Scientific preparations for teaching purposes	2,000
Coal-tar colours, including by-products .	183,000	Solid soaps	59,000
Solutions of coal-tar printing	7,000	Wool fats and oils . .	17,000
Material for ligatures .	16,000	Other purposes . . .	24,000
Other substances enumerated under (d), section 4, of the regulations	541,000		

Alcohol for Burning Purposes. One of the first uses of alcohol other than for drinking purposes was for burning, either for illuminating or for heating purposes. Alcohol itself gives a non-luminous flame, but this can be rendered luminous by the addition of hydro-carbons. More recently the incandescent mantle has been used with success with a mixture of alcohol vapour and air as fuel. The clean smokeless flame of alcohol renders it ideal for heating

purposes on a small scale, where the expense is not prohibitive. The question of motor fuel forms the subject of a separate chapter.

Alcohol as a Solvent. This forms the basis of some of the most important technical and domestic uses of alcohol. It will be seen from the table showing the industrial applications in this country that varnishes, polishes, lacquers, finish, stains and a number of other applications in which the alcohol is used as a solvent, account for the bulk of the industrial alcohol which is consumed. Apart from these applications, the solvent properties of alcohol make it an important adjunct to fine chemicals of all kinds. Thus it is used for the purification of drugs and other fine chemicals by crystallization; it enters similarly as a solvent into the manufacture of dyes. It is used further to extract the valuable medicinal materials from the roots, barks, etc., which contain them. In the manufacture of soap, it is used as a solvent to produce a transparent effect.

Alcohol mixed with ether (which is itself made from alcohol) forms a valuable solvent for nitro-cellulose, and this renders it of importance for celluloid and explosives manufacture. In photography it is used for the collodion films of the sensitive plates.

The solvent properties of alcohol render it valuable for the removal of carbon deposits in the cylinders of internal combustion engines, since it extracts the resinous material which binds the carbon and so causes it to cake. Alcohol enters also into the composition of numerous liniments, toilet waters, perfumes, flavouring extracts, liquid soaps, disinfectants, etching solutions, soldering fluxes, etc.

Chemical Syntheses Employing Alcohol. The processes to be considered under this heading are—

(a)—Dehydration of alcohol.

(b)—Oxidation of alcohol.

- (c)—Formation of esters.
- (d)—Action of halogens on alcohol.
- (e)—Manufacture of ethyl anilines.
- (f)—Manufacture of ethyl mercaptan.

(a) DEHYDRATION OF ALCOHOL

The abstraction of water from alcohol leads to the successive formation of ethyl, ether, and ethylene (Chapter II).

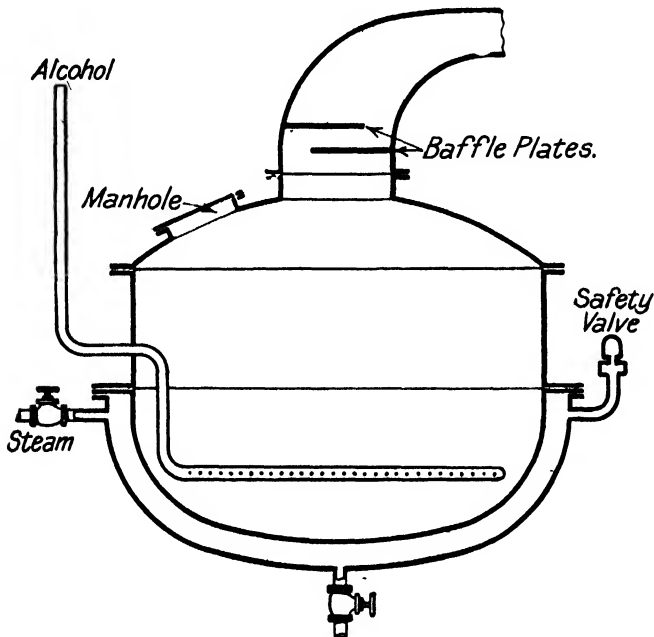


FIG. 9.—SIMPLE APPARATUS FOR MANUFACTURE OF ETHER.

(1) *Ethyl ether* (sulphuric ether) $(\text{CH}_3\text{CH}_2)_2\text{O}$. Nine parts of concentrated sulphuric acid and five parts of 90 per cent. alcohol are heated together in a cylindrical pan of lead-lined iron provided with a steam jacket (Fig. 9). Alcohol is then added continuously, the temperature being maintained at 130° to 140°C . If the temperature is too high, ethylene is formed. The ether distils over continuously, and is passed through a lead-lined scrubber to remove the sulphur dioxide, which always accompanies it owing to decomposition of the

sulphuric acid. The ether vapour may also be dried by passing it through a column of calcium chloride. Further details of the preparation are given in Ullmann's *Enzyklopädie der technischen Chemie*.

A modern improvement of the plant for ether manufacture is Barbet's apparatus.* In this, a tower is divided into sections containing distributing plates, and the whole tower is kept hot by steam coils. Sulphuric acid is fed in at the top, and alcohol part-way down the tower. On mixing, the sulphuric acid and alcohol give rise to ether, and a mixture of ether and alcohol vapour passes up the tower, meeting fresh sulphuric acid, which converts the remainder of the alcohol to ether. This is then led to a condenser in which it is liquefied.

Norton and Prescott† find 140° to 145°C to be the temperature at which the optimum conversion takes place. The yield is stated to be improved somewhat by the addition of a little ferric chloride, or stannous sulphate.‡ Benzene sulphonie acid has been used instead of sulphuric acid, to avoid the formation of sulphur dioxide.§

Theoretically the process is absolutely continuous, the sulphuric acid acting as a catalyst through the formation and decomposition of ethyl hydrogen sulphate. In practice, side-reactions occur, which make it necessary to interrupt occasionally the working of the process. The chief by-products are ethylene, sulphur dioxide, ethane sulphonie acid, and the so-called "oil of ether," which contains ethers, ketones, and hydrocarbons (ethyl-amyl-ether, diamylene, ethyl-amyl-ketone, methyl-hexyl-ketone, etc.). The ether is purified by fractional distillation and treatment with calcium chloride and wood charcoal. If very pure ether is required, it may be treated, before distillation, with metallic sodium or phosphorus pentoxide. The pure compound boils at 35°C , and has a sp. gr. of 0.720 at 15°C .

Ether is a valuable solvent for many organic substances. Its chief use is in admixture with alcohol as a solvent for nitrocelluloses for collodion, propellant explosives, etc. It is used also as a solvent in various technical processes, as a local anaesthetic, and in ice-making.

(2) *Ethylene*, $\text{CH}_2\text{:CH}_2$. This is made in the laboratory from alcohol and sulphuric acid at 160 to 170°C ., and passed through sulphuric acid and caustic soda scrubbers to remove alcohol, ether, and sulphur dioxide. This method has been superseded on the large scale by methods in which the alcohol vapour is either bubbled through syrupy phosphoric acid in iron pots

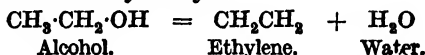
* French Pat. 479,435 of 1914; Brit. Pat. 100,406 of 1916.

† *Amer. Chem. J.*, 1884, Vol. 6, p. 243.

‡ Oddo, *Gazz. Chim. Ital.*, 1901, Vol. 31, I, p. 316.

§ Krafft, *Ber. deutsch. Chem. Gesell.*, 1893, Vol. 26, p. 2831; German Pat. 69,116.

at about 300°, or passed through heated tubes containing kaolin, which acts catalytically—



The water is condensed out as far as possible, and the gas is dried by means of moderately concentrated sulphuric acid, which must not be strong enough to absorb the ethylene.

The direct recovery of ethylene from coke-oven gas and coal-gas, and its possible application as a source of alcohol, have been considered in Chapter VI.

(b) OXIDATION OF ALCOHOL

This gives rise to acetaldehyde and acetic acid. More vigorous oxidation gives oxalic acid, whilst complete combustion gives water and carbon dioxide.

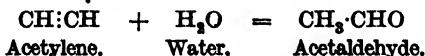
(1) *Acetaldehyde*, CH_3CHO . In the laboratory, the oxidation is effected by bichromate and sulphuric acid, but on the large scale catalytic methods are used, the alcohol decomposing according to the equation—



The best catalyst for this purpose is metallic copper at a temperature of 300° to 310°C. Nickel, cobalt and platinum are unsatisfactory, as they decompose the acetaldehyde to methane and carbon monoxide. Quartz powder may be used but requires a higher temperature.

The catalytic oxidation of alcohol may also be effected by air at ordinary temperature in presence of platinum-black or at higher temperatures in presence of metallic copper, charcoal, etc.

Acetaldehyde is used in the preparation of certain dyes and for making paraldehyde, which has some application in medicine. Apart from its production from alcohol, acetaldehyde may also be obtained from acetylene by passing the gas into water containing mercuric oxide and a weak acid—



(2) *Acetic Acid*, CH_3COOH . This is produced by the further oxidation of acetaldehyde. This oxidation is best effected catalytically, namely by passing oxygen or air into acetaldehyde containing a catalyst such as manganese acetate.

The direct oxidation of alcohol to acetic acid is carried out on a very large scale in the production of vinegar by means of micro-organisms (*bacterium aceti*). This is an enzymatic process and the enzyme can be separated from the living organism.* Nitrogenous materials and salts are necessary for

* Buchner, Meisenheimer, *Ber. deutsch. Chem. Gesell.*, 1903, Vol. 36, p. 634.

the nutriment of the bacteria. Ammonium acid phosphate and the corresponding sodium and potassium salts, also ammonium and magnesium sulphates are used in this connection, and beer and malt extracts, glucose, syrup, etc., are frequently added.

The annual output of vinegar in this country is given by Chapman* as 15 million gallons.

In Germany more than 3 million gallons a year of alcohol are used for making vinegar. The oxidation is carried out in cylindrical vats 2 or 3 metres high, and 1 to 2 metres in diameter, containing wood shavings resting on a perforated bottom and surmounted by a perforated disc. Access of air for the oxidation is provided by holes in the sides of the vat.

A pure culture of *bacterium aceti* is mixed with the first charge of alcohol, and this is delivered on to the top of the shavings. The alcohol is of about 6 to 10 per cent. strength, and the temperature 25° to 35°C. Heat is evolved by the oxidation and must be removed by keeping the temperature of the room from 5° to 10°C below that of the vat. A temperature of 50°C. kills the micro-organisms.

The product contains 4 to 6 per cent. of acetic acid and a little unchanged alcohol. If the conversion be carried too far, some of the acetic acid itself is decomposed. The yield is 80 to 90 per cent. of the theoretical, a good deal of alcohol being lost by evaporation. The impurities consist mainly of extractive matter.

Acetic acid is used in a dilute condition as vinegar for domestic purposes and for preserving. It is also used on a large scale for making white lead and lead acetate (sugar of lead). It can be concentrated by treatment with sulphuric acid and distillation, and in the pure state forms a pungent-smelling liquid (glacial acetic acid) which boils at 118°C. and freezes at 17°C. This concentrated form of acetic acid is used for making various esters such as ethyl acetate, amyl acetate, etc. The acetic acid for these purposes is, however, generally obtained from the distillation of wood.

Acetic acid enters into the preparation of various drugs (acetanilide, phenacetine, aspirine, etc.) and of dye-stuffs.

(c) FORMATION OF ESTERS

The alcohols can react with acids to form ethereal salts or esters (Chapter II). The methods given below for ethyl esters are, in general, also applicable to methyl esters.

Ethyl chloride, $\text{CH}_3\text{CH}_2\text{Cl}$. Alcohol is mixed with concentrated hydrochloric acid in a lead-lined autoclave, and heated gradually. The temperature is ultimately raised to 130°C. for some hours. After cooling, the ethyl chloride is distilled

* Cantor Lectures, 1920.

off and condensed (b.p. $12.5^{\circ}\text{C}.$). Any alcohol and hydrochloric acid present in the ethyl chloride are washed out with water containing a little alkali. The product is rectified, the vapour being scrubbed with concentrated sulphuric acid to remove impurities. If a catalyst such as zinc chloride be added, the reaction proceeds at a lower temperature.

Ethyl chloride is used as a local anaesthetic, and as a means of introducing the ethyl group into amines for use in dyes, etc.

Ethyl bromide, $\text{CH}_3\text{CH}_2\text{Br}$. One part by weight of concentrated sulphuric acid is run slowly into one part by weight of alcohol, the mixture being kept cool. Two parts of sodium bromide are then added, and the whole is gradually heated. Ethyl bromide (b.p. $39^{\circ}\text{C}.$) distils over, and is purified by washing with dilute soda, dried with calcium chloride, and redistilled. It is liable to contain a little ether, and this can be removed by treatment with concentrated sulphuric acid. Ethyl bromide is used as an anaesthetic, alone or with ethyl chloride or methyl chloride. It is also used, like ethyl chloride, for the introduction of ethyl groups.

Ethyl iodide, $\text{CH}_3\text{CH}_2\text{I}$. This is made from alcohol, iodine, and red phosphorus. One part of red phosphorous is mixed with five parts of alcohol, and ten parts of iodine are added gradually. After standing for some hours, the mixture is heated under a reflux condenser for two hours and then distilled. Ethyl iodide can also be made from alcohol and concentrated hydriodic acid. It boils at $72^{\circ}\text{C}.$

Ethyl nitrite, $\text{CH}_3\text{CH}_2\text{ONO}$. This is not usually prepared in the pure state. An alcoholic solution is made readily by adding a mixture of alcohol and dilute sulphuric acid to a solution of sodium nitrite in a freezing mixture. The liquid is then distilled, the distillate is neutralized with magnesia and distilled again. Ethyl nitrite mixed with alcohol is used as "sweet spirit of nitre" in pharmacy.

Ethyl nitrate, $\text{CH}_3\text{CH}_2\text{ONO}_2$. This is made from alcohol and nitric acid, but oxidation occurs if any nitrous acid is present, hence in practice urea is added to destroy the nitrous acid. The acid and alcohol are brought together slowly at a low temperature and distilled carefully, as the compound explodes if over-heated. It boils at $87^{\circ}\text{C}.$ and serves for the preparation of hydroxylamine and other products.

Monoethyl sulphate (ethyl hydrogen sulphate, sulphovinic acid), $\text{CH}_3\text{CH}_2\text{HSO}_4$. Alcohol and sulphuric acid are mixed gradually, the mixture being kept cool. The mixture is heated to $100^{\circ}\text{C}.$ for about four hours and cooled. Ice is added, and the ethyl hydrogen sulphate is neutralized with calcium carbonate. Any unchanged sulphuric acid is thus precipitated as calcium sulphate. The solution is concentrated and used as such or converted to the potassium salt by adding potassium carbonate. If the free acid is required, the barium or lead salt is made first and treated with the equivalent quantity of

sulphuric acid. The solution is then evaporated in a vacuum. Monoethyl sulphate is used for various ethylations.

Diethyl sulphate, $(\text{CH}_3\cdot\text{CH}_2)_2\text{SO}_4$. This is made from alcohol and fuming sulphuric acid by mixing these at a low temperature (-10 to -20°C). The diethyl sulphate is distilled off in a good vacuum. The compound can also be obtained by distilling sodium monoethyl sulphate in a good vacuum. Another method is to pass chlorine and sulphur dioxide into alcohol. The sulphuryl chloride reacts with the alcohol to form diethyl sulphate. A method of preparation of diethyl sulphate from ethylene and sulphuric acid has been described by Sidgwick and others.*

Diethyl sulphate boils at 208°C . with decomposition at atmospheric pressure and is poisonous. It is used for various ethylations.

Esters of organic acids. The general method for the preparation of these is to mix the alcohol and acid with sulphuric acid, and heat for some hours under a reflux condenser. The acid layer is then separated, and the ester is agitated with a solution of sodium carbonate to remove the dissolved acid. After again separating, the ester is distilled fractionally. Any alcohol present can be removed by shaking with concentrated salt solution, in which the esters are almost insoluble.

Esters can also be prepared by catalysis.† The mixed vapours of the alcohol and acid are passed over heated titanium dioxide or thoria at a temperature of 150 to 300°C .

Esters are largely used in perfumery and for essences and medicinal purposes, also to some extent as solvents. Examples of ethyl esters of organic acids are ethyl formate, acetate, butyrate, benzoate, and aceto-acetate. The last mentioned is made from ethyl acetate by the action of sodium.‡ It is of importance as the material from which antipyrine (dimethyl phenyl pyrazolon) is made and enters also into the manufacture of dyes.

(d) ACTION OF HALOGENS ON ALCOHOL

(1) *Chloral* (trichloroaldehyde), $\text{CCl}_3\cdot\text{CHO}$. This is made by passing chlorine into absolute alcohol, at first in the cold and then raising the temperature gradually to the boiling point. When the liquid is saturated with chlorine, the chloral-alcoholate which is formed is shaken with concentrated sulphuric acid to liberate the chloral. This is separated as a liquid and rectified

* Brit. Pat. 157, 578, cf. also Plant and Sidgwick, *J. Soc. Chem. Ind.*, 1921, Vol. 40, 14 T.

† Sabatier and Mailhe, *Comptes rendus*, 1911, Vol. 152, pp. 494, 1044.

19‡ For manufacturing process, see Cobenzl, *Chem. Zeit.*, 14, Vol. 38, p. 365.

over calcium carbonate. It boils at 97.5°C . When treated with water, chloral is converted to chloral hydrate, $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$, and most of it is used in this form. One part of water is added gradually to 8 parts of chloral and the hydrate is crystallized from benzene or other solvents. It is a solid crystalline compound which melts at 53°C . and boils with dissociation at 97.5°C .

(2) *Chloroform*, CHCl_3 . This is made by the action of bleaching powder on alcohol or acetone. The chlorine acts partly as an oxidizing agent, converting the alcohol to aldehyde, and partly as a chlorinating agent, converting this to trichloroaldehyde (chloral) which is decomposed by the lime to chloroform (Chapter II). The alcohol is placed in a large cylindrical iron vessel and diluted with water. Bleaching powder is then added, the contents of the vessel being kept agitated by a stirrer. When all of the bleaching powder has been added, the temperature is raised to 40°C ., and the reaction proceeds with gentle evolution of heat. The temperature is not allowed to exceed 60°C . The contents of the still distil over and are condensed, washed, and rectified.

A continuous process has also been devised, the apparatus being somewhat similar to the Coffey still (Chapter IV).

Chloroform boils at 61°C . and is used largely as an anaesthetic. It decomposes slightly under the action of air and light, forming carbonyl chloride, which is very poisonous. To prevent this, a little alcohol is added to the chloroform; this reacts at once with any carbonyl chloride and renders it innocuous.

Bromoform, CHBr_3 , is the bromine analogue of chloroform, and is made from alcohol by the action of bromine and alkali. It has a limited application as an anaesthetic.

Iodoform, CHI_3 , is the corresponding iodine compound. It is obtained readily by warming a mixture of alcohol, iodine, and sodium carbonate solution. The iodoform separates out as an insoluble precipitate. The iodine which passes into aqueous solution as iodide, etc., is recovered by chlorine, bichromate or other means. Combined processes are also in use which set free the iodine and render it available to react with more alcohol. The preparation of iodoform is also carried out electrolytically. Iodoform is a yellow solid, melting at 119°C . and is used extensively as an antiseptic.

(c) ETHYL ANILINES

Methyl and ethyl derivatives of aniline are much used in the manufacture of dye-stuffs.*

Monoethyl-aniline, $\text{C}_6\text{H}_5\text{NHC}_2\text{H}_5$, is made by heating aniline hydrochloride with alcohol in an autoclave for some hours at 180°C . It is a liquid boiling at 206°C .

Diethyl-aniline, $\text{C}_6\text{H}_5\text{N}(\text{C}_2\text{H}_5)_2$, is prepared in similar manner. An improved method is to heat aniline hydrobromide with

* Cain, *The Manufacture of Intermediate Products for Dyes*.

alcohol. The compound can also be prepared by heating aniline and alcohol with a little iodine. It is a liquid boiling at 216.5°C . and is used in making Brilliant Green, Patent Blue V, and Ethyl Purple 6B.

The sulphonic acids of these amines are also made for conversion to the ethyl-aminophenols which are used for making Rhodamine dyes.

Benzyl ethyl aniline is used in the manufacture of Xylene blue AS, Erioglaucine, and other dyes.

Ethyl toluidines are made similarly, and are likewise used in the manufacture of dyes (Cyanol, New methylene blue, etc.).

(f) ETHYL MERCAPTAN, $\text{C}_2\text{H}_5\text{SH}$

This is made by the action of potassium hydrogen sulphide on calcium ethyl sulphate (prepared from alcohol as described above). The mixture is distilled (b.p. 36°C .) and further purified by caustic soda, which dissolves the mercaptan but leaves the diethyl sulphide unchanged. The mercaptan is liberated from the alkaline solution by addition of acid.

Ethyl mercaptan has a very obnoxious odour. It is not used directly, but is valuable for the preparation of the hypnotics sulphonal, trional and tetronal.

Alcohol and National Defence. The importance of alcohol for war purposes was realized during the European War, when large quantities were used for munitions. The chief uses are the following.

Explosives. A mixture of alcohol and ether (which is made from alcohol) forms a solvent for certain forms of nitrocellulose, and was used as a gelatinizer for a very large proportion of the propellant explosives used in the war.

Acetone, which is another solvent largely used in the manufacture of propellents, may also be obtained from alcohol, when necessary, by oxidizing the alcohol to acetic acid, as described earlier, and thence to acetone by the catalytic action of metallic acetates at high temperatures.

In high explosives, alcohol is used for crystallizing compounds such as trinitrotoluene, when these are required in a pure condition, but may be superseded by methods in which the impurities are extracted by aqueous solutions of suitable salts.

Mercury fulminate, which is used largely for

detonators, is made from alcohol, nitric acid and mercury. The mercury is put into a glass flask and the nitric acid is added. When the mercury is dissolved, the solution is poured into alcohol. The mixture becomes hot, and after a time mercury fulminate separates out and is purified by washing.

Aircraft. Alcohol enters into the composition of the dopes used for aeroplane wings. It has not up to the present been used largely as a fuel in aeroplane engines, but the experimental results quoted in Chapter VIII indicate that this use may be of importance for the future of national defence.

Motor transport. Here again the importance of alcohol as a potential motor fuel indicates the necessity of providing for supplies which could be used in case of national emergency.

Poison gas. The well known "mustard gas," used at first by the Germans, and later by the Allies, is made from ethylene and sulphur monochloride. Ethylene is made from alcohol (p. 80) and large quantities of alcohol were used in this way during the war. Alcohol also enters into the preparation of other toxic substances.

As an indication of the quantities of alcohol which may be consumed for such purposes as the above, it is stated by Tunison* that 52½ million (American) proof gallons of alcohol were used by the United States in 1918 for war purposes.

It is impossible to foresee what new developments may take place in methods of warfare, but it appears certain that a material which has such manifold uses as alcohol will play an important part in many directions, if this country is again called upon to take part in a war such as that of 1914 to 1918.

* *J. Frankl. Inst.*, 1920, Vol. 190, p. 373.

CHAPTER VIII

ALCOHOL FOR POWER PURPOSES

The Need for Petrol-Substitutes. The interest which alcohol has attracted as a possible source of power is of recent growth. Up to the present, alcohol has been used only to a very limited extent for motors, but in view of the increasing shortage and rising price of petrol, the question of an alternative liquid fuel is becoming more and more urgent.

In 1905 a Government Departmental Committee on Industrial Alcohol reported that spirit was not used in this country for motor vehicles, and that as, at that time, the price of petrol was about half that of methylated spirit, the Committee considered that close investigation of the matter might be delayed until such time as there might be an approximation between the prices of petrol and spirit sufficient to create a practical alternative of choice between the two.

In 1904, petrol was 10d. per gallon ; in 1906 it had risen to 1s. 4d. ; in 1914 to 1s. 9d. ; and in 1921 it is 3s. 5½d. per gallon. This represents an enormous additional charge on all power purposes using internal combustion engines, and it is no longer a matter of *laissez faire* but of taking active steps to provide a cheaper substitute ; the more so as it is not merely a question of price, but also of limitations in the world's supply of petrol.

The total petroleum production of the world is equal in quantity to about one-quarter of the coal output of the British Isles. Petroleum is thus by no means an abundant fuel as compared with coal, and the petrol forms only a small fraction of the petroleum. The increasing consumption of petrol

in the United States has brought about a great decrease in the quantity available for export from that country and, in 1911, the U.S.A. Government reported that the probable life of the older fields was only about 35 years, allowing for the increasing demands.* Considerable quantities are even now being imported into the United States from Mexico. New oil-fields may be discovered, but it will take time to develop them, and by that time existing fields may have ceased to produce; meanwhile, the demand will have increased far beyond the present requirements.

At the outbreak of war there were in Great Britain about 440,000 motor vehicles, including about 30,000 of the heavy commercial type and some 1,700 were being added weekly to that total.†

The Shell Company stated, in an open letter to the President, Board of Trade‡—

“It is unquestionable that the world demand for petrol even at the present time exceeds the supply, and the great shortage already existing in other European countries is evidence of this fact. We entirely agree that every endeavour should be made to foster the production of power-alcohol, and other motor fuels of all kinds both in the British Empire and throughout the world.”

Possible Substitutes for Petrol. The possible alternatives to petrol are few; in some cases coal-gas can be used§; benzol is being used to the limit of what is available, but the demand for power-benzol forms a serious handicap to the use of benzol as a starting point for numerous other industrial applications (dyes, etc.), and its available quantity is not such as to afford a full solution to the problem. It is stated|| that whereas the retail price of benzol is

* Tweedy, *Industrial Alcohol*, pp. 7, 8.

† Tweedy, *Industrial Alcohol*, p. 5.

‡ *Times*, 17th March, 1920.

§ Compare Memo. of Fuel Research Board, July, 1920.

|| *Chem. Trade J.*, 1921, Vol. 68. 166.

3s. 8d. the cost of making crude benzol is only 10·1d. and of refining 4·55d. per gallon, taking the average of six factories. Bury and Ollander* give the national requirements of motor spirits as 160 million gallons per annum, against which we have only 30 millions approximately of benzol plus the shale fuels, as home-produced fuels, and the remainder has to be imported (in the form of petrol) from distant countries which may or may not remain friendly.

Having taken into account the possibilities and limitations of benzol, we are thrown back on to alcohol as practically the only other volatile combustible liquid which can be made available in large quantities. It may be that new syntheses will render methyl alcohol available in large quantities, but we cannot safely build upon this possibility, and the toxic effect of methyl alcohol in its commercial form would appear to be a serious drawback.

In June, 1919, the Government Committee on Power Alcohol reported† that the time had come for action by the Government to ensure close investigation of the questions of production and utilization, in all their branches, of alcohol for power and traction purposes, and made recommendations as to experimental and practical development work. They recommended also that various excise restrictions should be removed and other facilities given "in advance of the time when an acute recurrence of high prices for motor-fuels may otherwise call for action too late for it to be effective." In May, 1920, the Empire Motor Fuels Committee was formed. This committee gave special prominence to power alcohol in its report of February, 1921.

In a foregoing chapter we have considered the possibilities of extending the sources of supply of alcohol, and in the present chapter we have to review

* *Cleveland Inst. of Engineers*, 1919-20, p. 45.

† *Cmd.*, 218.

the evidence bearing on the practical suitability of alcohol as a liquid fuel for internal combustion engines.

Use of Power-Alcohol Abroad. The Departmental Report on Industrial Alcohol in 1905 indicated that, even at that time, alcohol was in use to some extent in France and Germany for agricultural engines.

In February, 1915, Prof. V. B. Lewes stated that when the Russians over-ran Galicia, and thus shut off this source of petrol-supply from Germany, every motor car in the German Empire was adapted to the use of alcohol.

Natal has been producing power-alcohol for several years, and the output in 1919 was about 400,000 gallons.* Australia is following this example, using raw materials from New Guinea. One of the most important features of the Australian tariff of 1920 was the removal of the excise duty of 1s. per gallon on industrial denatured spirit. The Minister of Customs stated that the Australian Government recognized the possibilities of power-alcohol and was desirous of encouraging it. The immediate result of the Minister's statement was the formation of a Company to manufacture motor spirit on a large scale.† Extensive preparations are also stated to be on foot to make industrial alcohol in New Zealand.‡ According to Major-Gen. Sir John Fowler§ the use of power-alcohol is increasing in the United States.

Comparison of Petrol and Alcohol. Alcohol differs from petrol in that it is a definite chemical compound of fixed properties. Different supplies of petrol may vary considerably in their volatility and composition. For this reason, it should be possible to standardize

* *J. Soc. Chem. Ind.*, 1920, Vol. 39, 435R.

† *Times Trade Suppl.* 12th June, 1920.

‡ *Chem. Trade J.*, 1920, Vol. 67, p. 414.

§ *Times Trade Suppl.*, 3rd July, 1920.

the working conditions of a motor more closely in the case of alcohol than in that of petrol.

The following pages give a comparison of the physical and chemical characteristics of petrol and alcohol in so far as this is of importance in considering alcohol as a substitute for petrol.

Specific gravity and Weight per gallon.

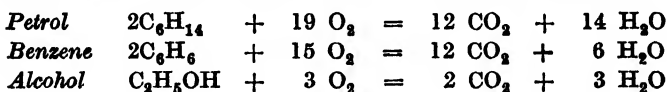
		Sp. gr.	Lb. per gall.
Petrol	. . .	0.684 to 0.750	6.84 to 7.5
Benzol	. . .	0.897	8.97
Alcohol	. . .	0.800	8.00

Miscibility with water. Alcohol mixes in all proportions with water. A small quantity of water finding its way into a petrol tank is very objectionable, whereas in the case of alcohol a little water will simply mix with the alcohol and will not materially affect its utility.

This miscibility with water enables an accidental fire of alcohol to be extinguished by water much more readily than a petrol fire.

Ignition temperature. This was determined by Dixon* who found for alcohol 510°-515°C. in oxygen and 595°-600°C. in air; for pentane 550°C. and 560°-570°C.; and for ether 240°C. and 580°C., respectively.

Proportion of air required for combustion. If we take petrol as approximately C_6H_{14} we have for the combustion of petrol, benzene, and alcohol respectively the following equations—



From these, the volumes of oxygen and the corresponding volumes of air necessary for the combustion of one volume of fuel vapour are found to be as follows—

	Oxygen	Air
Petrol	9.5	45
Benzene	7.5	36
Alcohol	3.0	14

In practice, the quantities of air admitted would be about 50 per cent. greater than those calculated. It is probably due to the large excess of inert nitrogen which is necessarily present in the combustion of petrol, and to the difficulty of ensuring

* Conference of Motor Transport Council, *J. Soc. Chem. Ind.*, 1920, Vol. 39, p. 355R.

uniform admixture, that a large proportion of the carbon and hydrogen escapes combustion. This must be accounted a point in favour of alcohol as compared with hydrocarbon fuels. In some cases 80 per cent. of the hydrogen and 40 per cent. of the carbon in petrol are thus wasted.

Range of explosive mixtures. Mixtures of petrol vapour and air will not explode if the petrol vapour is less than 2 per cent. by volume. Mixtures containing 2 to 5 per cent. of petrol are capable of explosion, but mixtures containing more than 5 per cent. are incapable of explosion because they are too rich in petrol. Theoretically, the mixture should contain 2.2 per cent. of petrol vapour (by volume) for complete combustion.

In the case of alcohol the theoretical mixture contains 6.5 per cent. of alcohol vapour, and the practical range is from 4 to 13.6 per cent. by volume. Thus alcohol has a much wider latitude than petrol, and the air supply need not be adjusted so closely.

Heat and energy value. The calorific value of a fuel is of importance as an indication of the amount of potential chemical energy which it contains. A comparison of alcohol and petrol gives the following figures—

	British Thermal Units	
	per lb.	per gallon
Pure ethyl alcohol	12,700	102,000
Methyl alcohol	9,600	77,000
Methylated spirit (Sp. gr. 0.815)	11,160	94,500
Petrol (Sp. gr. 0.684)	20,923	143,000

The heat energy of petrol is seen to be much higher than that of alcohol. From a chemical point of view this is not surprising, as alcohol contains a hydroxy-group, and thus carries a burden of useless oxygen.

On the basis of heat value, the evidence would appear, on a *prima facie* consideration, to be strongly against alcohol as a fuel. This is, however, compensated by the greater efficiency in the conversion of heat energy to work in the case of alcohol. Lewes* has shown that the efficiency in the case of alcohol is 28 per cent., against 16.5 per cent. in the case of petrol. This is because the alcohol is much more completely combusted than the petrol. The actual quantities of petrol and alcohol consumed in two 8-h.p. engines running under parallel conditions were as follows—

	Per h.p.-hour	
	grams	cu. cm.
Petrol	340	498
Methylated spirit	375.5	462

The more complete combustion of alcohol also has the effect

* *Liquid and Gaseous Fuel*, p. 302.

of making the exhaust from the engine smokeless and almost inodorous.

Vapour pressure. A comparison of the volatilities of alcohol and hydrocarbons at ordinary temperatures is of importance. Fig. 10 shows the vapour pressures of methyl and ethyl alcohol as compared with those of hydrocarbons of the paraffin series and the benzene group. The important point is that the vapour

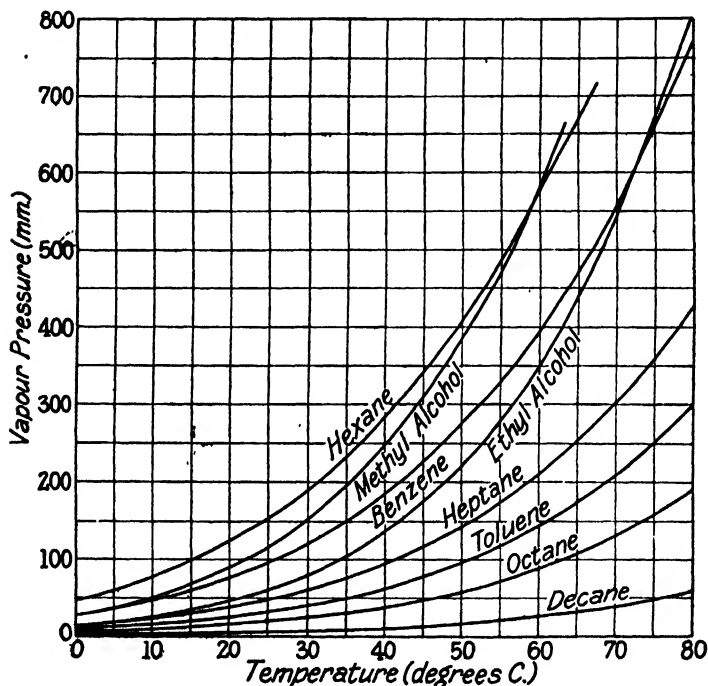


FIG. 10.—VAPOUR PRESSURE—TEMPERATURE CURVES FOR ALCOHOLS AND HYDROCARBONS.

pressure of the alcohols decreases much more as the temperature falls than those of the hydrocarbons. Although alcohol boils at about the same temperature as benzene, the vapour pressure of benzene at 10°C. is twice as great as that of alcohol. Similarly, petrol of about the same boiling point as alcohol is much more volatile than the latter at ordinary temperature. The flash-point of alcohol is about 65°F (17°C) which is much higher than that of petrol or benzene.

The consequence of this is that it is very difficult to start an engine on alcohol, especially in cold weather, since even the saturated alcohol vapour is not explosive below 20°C. If alcohol is used alone, special means must be used to start the engine, such as a pre-heater for the carburettor*, or an arrangement whereby a small amount of petrol can be used at the start. This has led to the use of mixed fuels in which the alcohol is mixed with ether ("Natalite") or benzol, and it is probable that such mixtures will always be used in the case of power alcohol. Sidgwick† has examined the system benzene-alcohol-water at different temperatures. He also points out the low solubility of petrol in alcohol of 90 per cent. strength. The use of alcohol containing dissolved acetylene as a fuel has also been proposed to overcome the above difficulty.‡

Prof. H. B. Dixon undertook researches for the Committee on the Utilization of Power-Alcohol appointed in 1918 by the First Lord of the Admiralty, and found that a mixture of alcohol and ether with hexane or benzene gave good results. A pre-heater should be used with alcohol on account of its relatively high heat of evaporation (p. 15).

Alcohol, being less volatile at ordinary temperatures than petrol, is safer for storage, but if mixed with ether, acetylene, etc., to overcome the difficulty of starting motors, the danger of volatility will of course be increased.

Rate of burning. Researches have been made by Prof. H. B. Dixon on the ignition temperatures and rates of burning of the different motor fuels§. He found that the alcohol flame starts more rapidly but the rate is not maintained, and thus alcohol takes longer than petrol to burn to an explosion. For this reason, an engine using alcohol or alcohol-benzene should have a higher compression and a longer stroke than a petrol engine. This necessitates some modification in the design of motors to obtain the best results with alcohol.

A Committee of the Australian Commonwealth Advisory Council on Science and Industry|| states that the main alterations necessary for an alcohol engine are the following—

(a) An increased compression from 75 lb. per sq. in., which is the average for petrol engines, to about 180 lb. per sq. in., both above atmospheric pressure.

(b) Pre-heating of either the fuel or the air or a mixture of fuel and air.

* See article on The D.C.L. Carburettor, *Daily Telegraph*, 5th May, 1921.

† *J. Chem. Soc.*, 1920, Vol. 117, 1397.

‡ Brit. Pat. 112,741 of 1917.

§ Conference of Imp. Motor Transport Council, *J. Soc. Chem. Ind.*, 1920, Vol. 39, p. 355R.

|| C. 7963, 1917.

(c) An increase in the area of the fuel jets and fuel supply pipes.

Heriot* stated that an alcohol-air mixture could be compressed with safety in the cylinder to 200 lb. per sq. in., whereas the limit for petrol-air was 80 lb. per sq. in.

Catalytic decomposition of alcohol at high temperatures. The saturated hydrocarbons which form the constituents of petrol are scarcely affected chemically by heat in absence of air or oxygen. Alcohol differs from these hydrocarbons in that it undergoes decomposition in several different directions when heated to 300°C. or more (compare Chapter II). The nature of the decomposition is largely determined by the catalytic action of the solid surfaces with which the alcohol vapour is in contact. The main decompositions are the following—

- (i) $\text{CH}_3\cdot\text{CH}_2\cdot\text{OH} = \text{H}_2 + \text{CH}_3\cdot\text{CHO}$ (aldehyde)
- (ii) $\text{CH}_3\cdot\text{CH}_2\cdot\text{OH} = \text{H}_2\text{O} + \text{CH}_2\cdot\text{CH}_2$ (ethylene)
- (iii) $2\text{CH}_3\cdot\text{CH}_2\cdot\text{OH} = \text{H}_2\text{O} + (\text{CH}_3\cdot\text{CH}_2)_2\text{O}$ (ethyl ether)
- (iv) $\text{CH}_3\cdot\text{CH}_2\cdot\text{OH} = \text{CO} + \text{H}_2 + \text{CH}_4$ (methane)

The first of these is favoured by metallic copper, oxides of manganese, tin, cadmium, etc. The second is induced by alumina, thoria, etc., and is frequently accompanied by some formation of ether as in (iii). The fourth usually takes place at higher temperatures. A comprehensive investigation of these reactions was made by Sabatier and Mailhe.†

Apart from the above products, ethane, acetylene, formaldehyde, ether, benzene, naphthalene and other compounds have been found.

Among the catalysts which bring about decomposition are pumice, silica, gypsum, kaolin, charcoal, graphite, zinc, nickel, cobalt and many other metals and their oxides—in fact almost every solid material appears to be capable of acting in some degree as a contact catalyst.‡ Thus the conditions in a motor will frequently be such as to induce a catalytic decomposition of the alcohol. In general, these decompositions will not play an important part, as the products will be at once further oxidized to carbon dioxide, but under certain conditions the aldehyde formed may oxidize to acetic acid and cause corrosion of the metal parts. Sometimes a little ammonia is added to neutralize the acid.

Practical Tests of Alcohol as a Motor-Fuel. It is more than twenty years since motor trials with

* *J. Soc. Chem. Ind.*, 1915, Vol. 34, p. 336.

† *Comptes rendus*, 1908, Vol. 146, p. 1376; Vol. 147, pp. 16, 106.

‡ For details see Beilstein, *Organische Chemie*, New Edn., I, p. 300.

alcohol as fuel were first made in Germany and France. In October, 1900, an important competition took place in France in which 62 motors were entered, of which 50 started and 35 finished the course of 76 miles. The fuels consisted of alcohol with 25 to 60 per cent. of petrol, and in a few cases alcohol alone. In 1909, further trials took place on a course of 167 miles. The results indicated that 1.78 gallons of alcohol gave the same result as 1 gallon of petrol.

Tests by Prof. Meyer, in 1901, on a 14-h.p. engine with alcohol and benzene gave a thermal efficiency of 24 to 25 per cent.*

In Germany a thermal efficiency of 31.6 per cent. was obtained with alcohol containing 13.9 per cent. of water.†

Systematic tests reported in Bull. No. 392, U.S. Geol. Survey, 1909, indicated that it was possible for any petrol engine to run on alcohol without material alteration in construction, and that 1 lb. of alcohol corresponded to 0.7 lb. of petrol (i.e. 1 gall. of alcohol to 0.83 gall. of petrol). When the engine was modified to give the best conditions for alcohol-fuel (larger passage-ways, etc.) the rate of consumption of alcohol fuel was practically the same as for gasoline. With the maximum compression for gasoline the available horse-power was increased about 10 per cent. by the use of alcohol. With the maximum compression for alcohol there was an increase of 30 per cent. over a gasoline engine of the same size, stroke, and speed. The maximum efficiency reached with gasoline was 28 per cent., and with alcohol 40 per cent.

Tests by Ormandy‡ gave the data shown in Table XIII for a 4-cylinder Maudslay engine running at 1,000 r.p.m. on different fuels.

* *Beama Journal*, 1920, Vol. 7, p. 93

† *Ibid.*

‡ *J. Gas Lighting*, 1913, pp. 124, 580.

TABLE XIII.—RELATIVE POWER AND RELATIVE VOLUME OF FUEL WITH PETROL, BENZOL, AND ALCOHOL MIXTURES.

Fuel used.	Relative Power.	Relative Volume of Fuel.
Petrol (sp. gr. 0.710)	100	100
Benzol	98.2	84.5
Methylated spirit 50%, benzol 50%	99	96.3
" " 67% " 33%	92	108.9
" " 75% " 25%	91.5	124.5

Trials described in *Die Treibmittel der Kraftfahrzeuge* (Berlin, 1917), gave the results shown in Table XIV.

TABLE XIV.—DISTANCE PER LITRE AND PER GALLON WITH VARIOUS MOTOR FUELS.

	Km. per Litre.	Miles per Gall.
Petrol	5.8	16.4
Benzol	7.1	20.0
Benzol 1 part, alcohol 1 part	7.5	21.2
" " " 2 parts	7.2	20.3
" " " 3 " 	7.0	19.7
" " " 4 " 	6.6	18.6
" " " 5 " 	6.0	16.9
Alcohol	5.4	15.2

Tests in Australia* indicated that the consumption of fuel was 50 per cent. greater in the case of alcohol

* Report of Executive Committee, C. 7,963, 1917.

than in that of petrol, but it appeared that if the design of the engine were modified to suit the alcohol-fuel, about equal volumes of the two fuels would be required to do the same work.

In the United States, the Post Office aeroplane mail service is being operated by an alcohol fuel,* and valuable information has been collected regarding the utility of alcohol. The consumption of alcohol-fuel in a series of flights was—

At 1,440–1,460 r.p.m. . .	15.9 gallons per hour
„ 1,475–1,480 „ . .	20.1 „ „
„ 1,500 „ . .	21.5 „ „
„ 1,520–1,525 „ . .	22.4 „ „

A comparison of alcohol-fuel with gasoline at different speeds gave the following data—

	Gallons per hour at—	
	1,475 r.p.m.	1,500 r.p.m.
Gasoline . . .	24	24.2
Alcohol-fuel . . .	20.1	21.5

The relatively low efficiency of gasoline was probably due largely to detonation (pp. 101, 102).

The alcohol-fuel was found to have advantages in giving less carbon formation and in avoiding forced landings due to fouled sparking-plugs.

Tests made by the London General Omnibus Co. These have been fully described by Sinkinson,† and Shave.‡ Bench tests gave the results shown in Table XV as an average of tests at all speeds on a 110 mm. × 140 mm. engine.

* Tunison *J. Frankl. Inst.*, 1920, Vol. 190, p. 417.

† *Beama Journal*, 1920, Vol. 7, p. 95.

‡ *Engineering*, 1920, Vol. 110, 623.

TABLE XV.—BENCH TEST DATA WITH PETROL AND BENZOL-ALCOHOL MIXTURE.

	Full Load.	Half Load.	Quarter Load.
<i>Petrol—</i>			
Thermal efficiency, per cent. . . .	15.7	11.0	7.2
B.Th.U. per b.h.p.-hr.	16,650	23,100	35,300
Lb. per b.h.p.-hr.	0.845	1.09	1.8
<i>50% Benzol-alcohol (compression 114 lb.)</i>			
Thermal efficiency, per cent. . . .	20.8	15.6	11.4
B.Th.U. per b.h.p.-hr.	12,200	16,300	22,500
Lb. per b.h.p.-hr.	0.81	1.08	1.49
<i>50% Benzol-alcohol (compression 123 lb.)</i>			
Thermal efficiency, per cent. . . .	22.8	16.9	10.6
B.Th.U. per b.h.p.-hr.	11,050	15,000	23,000
Lb. per b.h.p.-hr.	0.73	0.995	1.52

The fuel consumption per b.h.p.-hour was nearly constant for different speeds.

Tests on service gave the comparison shown in Table XVI between alcohol-mixtures and petrol.

TABLE XVI.—SERVICE DATA FOR FUEL CONSUMPTION OF MOTOR-BUSES, WITH PETROL AND VARIOUS ALCOHOL MIXTURES.

Alcohol Mixtures.				Petrol.		
Composition.		Total Mileage.	Miles per Gallon.	B.Th.U. per Mile.	Miles per Gallon.	B.Th.U. per Mile.
Alcohol.	Benzol.					
25	75	4,598	7.42	18,990	7.58	19,900
5	95	2,632	7.6	20,150	7.58	19,900
20	80	6,746	7.28	19,780	7.55	20,050
50	50	4,568	7.0	17,916	7.55	20,050

This shows that the 50 per cent. mixture gives the highest thermal efficiency.

In view of the promising results thus obtained a fleet of 14 motor-buses was provided with alcohol-benzol, and these gave very satisfactory results in

all weathers, on good and bad roads. The comparative results for 50 per cent. alcohol-benzol and for petrol were as in Table XVII.

TABLE XVII.—SERVICE COMPARISON BETWEEN PETROL AND ALCOHOL-BENZOL (50 %) MIXTURE.

	Miles per gallon.	B.Th.U. per mile.
<i>Summer conditions—</i>		
Alcohol-benzol 50%	7.0	17,816
Petrol	7.55	20,050
<i>Winter conditions—</i>		
Alcohol-benzol (50%)	6.05	20,650
Petrol	7.19	21,050

Both in summer and winter, the thermal efficiency of the alcohol fuel compares favourably with that of petrol but, when reckoned on the mileage per gallon, petrol shows to greater advantage.

Sidgwick* shows that in very cold weather there will be some danger of benzene freezing out from such mixtures.

Asiatic Petroleum Company's Investigations.—Important researches have been made by Ricardo† and by Tizard and Pye‡ on behalf of the Asiatic Petroleum Company. These cover a wide range of fuels, including alcohol.

Ricardo shows that the tendency of a fuel to detonate is very important. This tendency increases with the rate of burning, and a low rate of burning is very desirable. Owing to the high latent heat and low boiling point of alcohol the weight per charge is higher, and a higher power output is

* *J. Chem. Soc.*, 1920, Vol. 117, 1397.

† *Automobile Engineer*, 1921, Vol. II, 51, 92, 130.

‡ *Automobile Engineer*, 1921, Vol. II, 55, 98, 134.

obtained in consequence. If the compression is kept low enough to avoid any possibility of detonation, the efficiencies obtainable with different fuels vary only within small limits. Alcohol gives a slightly higher efficiency than hydrocarbons. Most petrol engines do not do themselves justice because they have too high a compression and are on the verge of detonation. When a fuel is substituted which has less tendency to detonate there is a gain in power and economy. Alcohol has very little tendency to detonate, and this explains to a great extent the higher efficiencies which have been observed by the use of alcohol as compared with petrol.

Tizard and Pye have made a comprehensive examination into the thermodynamics of the combustion of the different fuels. They also emphasize the importance of detonation. They show that a higher power is attainable with alcohol owing to the high latent heat. When working at a compression which is suitable for petrol, alcohol shows a lower power per unit weight, but in the case of alcohol it is possible to increase the power by working at a higher compression, which would cause detonation in the case of petrol.

General Observations on Alcohol Engines. In the various trials of alcohol fuel for motors and aeroplanes quoted above the general comments as to convenience, etc., confirm one another in showing that alcohol has advantages in cleanliness. The products of combustion do not clog the cylinder valves, and the sparking plugs do not easily become fouled, though in the motor-bus tests under winter conditions the sparking plugs tended to give some trouble owing to condensation of water. The exhaust gases are smokeless and nearly free from smell, provided the lubrication is good.

The general experience points to the importance

of high compression, and this becomes more necessary the higher the percentage of alcohol in the fuel. It is important to eliminate valve-pockets as far as possible, especially at high compressions. A vaporization-apparatus is desirable under winter conditions.

In general, therefore, it is seen that the petrol engine requires some modifications to suit it for alcohol-fuel. It is important to observe that, whereas the best conditions of working with petrol as fuel are known very fully, the work on alcohol-fuel is of a pioneering nature, and it is doubtful whether full justice has yet been done to alcohol. With further development the exact design of engine suitable for use with alcohol fuel will doubtless be evolved. Nevertheless, the results hitherto obtained show indubitably that if alcohol can be obtained in sufficient quantity at a satisfactory price, it will be able to take the place of petrol as a motor fuel, though it may be that the power developed per gallon of alcohol will not be quite as great as that of petrol.

APPENDIX

TABLE XVIII.—PERCENTAGE OF PROOF SPIRIT AND PERCENTAGE OF ALCOHOL BY WEIGHT AND BY VOLUME IN ALCOHOL-WATER MIXTURES OF VARIOUS SPECIFIC GRAVITIES AT 60°F (15.56°C).

Specific Gravity at 60°F (15.56°C).	Per-centage of Proof Spirit.	Percentage of Alcohol.		Specific Gravity at 60°F (15.56°C).	Per-centage of Proof Spirit.	Percentage of Alcohol.	
		By Weight.	By Volume.			By Weight.	By Volume.
0.7936	175.35	100.00	100.00	0.8460	150.97	80.79	88.12
0.7940	175.21	99.87	99.92	0.8480	149.80	79.98	85.46
0.7960	174.52	99.22	99.52	0.8500	148.62	79.17	84.78
0.7980	173.80	98.57	99.12	0.8520	147.43	78.35	84.11
0.8000	173.07	97.91	98.70	0.8540	146.23	77.53	83.42
0.8020	172.33	97.25	98.28	0.8560	145.01	76.71	82.73
0.8040	171.56	96.57	97.84	0.8580	143.78	75.88	82.03
0.8060	170.77	95.89	97.39	0.8600	142.54	75.05	81.32
0.8080	169.96	95.20	96.93	0.8620	141.28	74.22	80.61
0.8100	169.13	94.50	96.45	0.8640	140.02	73.39	79.89
0.8120	168.28	93.80	95.97	0.8660	138.74	72.55	79.16
0.8140	167.41	93.08	95.47	0.8680	137.46	71.72	78.43
0.8160	166.51	92.36	94.97	0.8700	136.16	70.88	77.69
0.8180	165.60	91.63	94.45	0.8720	134.84	70.04	76.94
0.8200	164.67	90.90	93.92	0.8740	133.53	69.19	76.19
0.8220	163.72	90.16	93.38	0.8760	132.19	68.35	75.44
0.8240	162.75	89.41	92.83	0.8780	130.86	67.51	74.68
0.8260	161.76	88.65	92.28	0.8800	129.50	66.66	73.91
0.8280	160.75	87.88	91.69	0.8820	128.14	65.81	73.13
0.8300	159.73	87.11	91.11	0.8840	126.77	64.96	72.34
0.8320	158.69	86.34	90.52	0.8860	125.37	64.10	71.55
0.8340	157.63	85.56	89.91	0.8880	123.97	63.24	70.75
0.8360	156.56	84.78	89.30	0.8900	122.56	62.38	69.95
0.8380	155.47	83.99	88.68	0.8920	121.14	61.52	69.14
0.8400	154.37	83.20	88.06	0.8940	119.70	60.66	68.33
0.8420	153.25	82.40	87.42	0.8960	118.26	59.80	67.50
0.8440	152.12	81.60	86.77	0.8980	116.81	58.93	66.67

Specific Gravity at 60°F (15·56° C).	Per-centage of Proof Spirit.	Percentage of Alcohol.		Specific Gravity at 60°F (15·56° C).	Per-centage of Proof Spirit.	Percentage of Alcohol.	
		By Weight.	By Volume.			By Weight.	By Volume.
0·0000	115·33	58·06	65·83	0·9540	67·48	32·09	38·57
0·0020	113·84	57·18	64·98	0·9560	65·09	30·90	37·20
0·0040	112·35	56·31	64·13	0·9580	62·60	29·66	35·79
0·0060	110·82	55·42	63·26	0·9600	60·03	28·39	34·33
0·0080	109·29	54·54	62·39	0·9620	57·33	27·06	32·79
0·0100	107·74	53·65	61·51	0·9640	54·51	25·68	31·18
0·0120	106·20	52·77	60·63	0·9660	51·53	24·23	29·48
0·0140	104·63	51·88	59·74	0·9680	48·38	22·71	27·69
0·0160	103·05	50·98	58·83	0·9700	45·14	21·14	25·83
0·0180	101·43	50·08	57·92	0·9720	41·77	19·53	23·91
0·0200	99·80	49·17	56·99	0·9740	38·35	17·90	21·96
0·0220	98·16	48·25	56·05	0·9760	34·87	16·25	19·98
0·0240	96·49	47·33	55·10	0·9780	31·42	14·61	18·00
0·0260	94·80	46·40	54·14	0·9800	27·99	12·99	16·04
0·0280	93·09	45·47	53·16	0·9820	24·66	11·42	14·13
0·0300	91·36	44·53	52·18	0·9840	21·44	9·91	12·20
0·0320	89·61	43·59	51·18	0·9860	18·34	8·46	10·51
0·0340	87·81	42·62	50·15	0·9880	15·38	7·08	8·80
0·0360	85·97	41·64	49·10	0·9900	12·53	5·76	7·18
0·0380	84·10	40·65	48·04	0·9920	9·82	4·51	5·63
0·0400	82·19	39·65	46·95	0·9940	7·24	3·31	4·14
0·0420	80·26	38·64	45·85	0·9960	4·73	2·17	2·71
0·0440	78·28	37·60	44·71	0·9980	2·33	1·07	1·34
0·0460	76·21	36·54	43·54	1·0000	0·00	0·00	0·00
0·0480	74·12	35·46	42·35				
0·0500	71·98	34·37	41·13				
0·0520	69·76	33·25	39·87				

Imperial gallon = 10 lb. avoirdupois.

Hectolitre = 22 Imp. galls. = 26·4 U.S.A. galls.

Imperial gallon = 1·2 U.S.A. galls. = 0·0455 hectolitre.

U.S.A. gallon = 0·8333 Imp. gall. = 0·0379 hectolitre.

The U.S.A. proof standard differs from the British standard as in Table XIX.

TABLE XIX.—BRITISH AND U.S.A. PROOF
SPIRIT STANDARDS COMPARED.

Per cent. of Proof Spirit.		Per cent. of Proof Spirit.	
Great Britain.	United States.	Great Britain.	United States
10	11·4	100	114·2
20	22·8	110	125·7
30	34·4	120	137·0
40	45·8	130	148·4
50	57·3	140	159·9
60	68·8	150	171·3
70	80·1	160	182·7
80	91·4	170	194·3
90	102·8		

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